



Rajeev Sah

Development and Optimization of Pilot Plant for Nutrient Recovery from Reject Water

Thesis submitted for examination for the degree of
Master of Science in Technology

Espoo 21.04.2019

Supervisor: Prof. Riku Vahala

Advisors: Prof. Anna Mikola

D Sc. (Tech) Surendra Pradhan

Author: Rajeev Sah

Title of thesis: Development and Optimization of Pilot Plant for Nutrient Recovery from Reject Water

Master programme: Water and Environmental Engineering. **Code:** ENG 29

Thesis supervisor: Prof. Riku Vahala

Thesis advisor: Prof. Anna Mikola & Surendra Pradhan

Date 21.04.2019 **Number of pages:** 52 pages, 3 pages **Language:** English.
appendices

Abstract

Reject water is produced by de-watering of anaerobically digested activated sludge in municipal wastewater treatment plants. This liquid contains a significant amount of, nitrogen (mostly as ammonium), phosphorus and suspended solids (organic matters) which needs to be removed before disposal. Currently, reject water is recirculated into the treatment system by Waste water treatment plants. This increases the ammonium concentration which also increase energy and resource consumption of the treatment process. A novel nutrient recovery technique (NPHarvest technique) has been developed in this study that can effectively remove the suspended solids, nitrogen and phosphorus from reject water and recover nutrient during the treatment process. The recovered nutrients are the raw materials for fertilizers. This work also supports circular economy. The purpose of this thesis was to design a batch process into the continuous process and construct a pilot plant in order to test and analyse the feasibility of the NPHarvest technique. This technique has a pre-treatment followed with the nitrogen recovery process. The nutrient recovery was performed using commercially available Liqui-Cel 3M membrane contactor to test its performance. This thesis presents a successful construction of pilot scale pre-treatment unit of NPHarvest technique for continuous flow. The pilot designed capacity is 100 l/hr. The experiment was carried out using a pilot plant in Viikinmäki wastewater treatment plants using their reject water. The optimal dose of coagulant (PAX XL 100), polymer (Super floc A120) and lime kiln dust (LKD) was 1.3 g/l, 1.3 mg/l, and 3.5 g/l, respectively. These doses are valid when the influent (reject water) suspended solid concentration is in range of 0.9 -1.6 g /l. The results from the pre-treatment showed that 82% suspended solid removal, 81% phosphorus recovery in sludge liquor. The Liqui-Cel 3M membrane contactor showed 78% ammonia recovery efficiency in the extraction solution. The NPHarvest technique operation cost was estimated to 3.18 €/m³ reject water or 5.10 €/kg NH₄-N recovery. Estimated for the energy used in maintaining the flow and chemical dose in NPHarvest technique was 5.4 kWh/ m³ of reject water.

Keywords: Coagulation, Flocculation, Ballasted sediment, Reject water, Pretreatment, Nutrient recovery, Sludge liquor, Feed-water, Extraction Solution

Acknowledgements

This master thesis has carried out from March 2018 to October 2018 in NPHarvest research group at the Aalto University of Water and Environmental Engineering. I would like to express my sincere gratitude and special thanks to my supervisor Prof. Riku Vahala for allowing me to be part of this project and all your help.

I would also like to thanks to my thesis advisor, Prof. Anna Mikola, “NPHarvest project manager” and my teacher who accepts me in this project and advice and direct throughout the work. In spite of busy schedules, you were all time to guide and correct my path. Surendra Pradhan, D Sc (Tech) has also involved as second advisor. He has been guiding and correcting me through the work. His contribution was very valuable and for which I express my gratefulness.

I am thankful to Mr. Ari Järvinen (Laboratory manager), and Antti Louhio (senior laboratory technician) for technical support and construction pilot, Mr. Juho Kaljunen (Doctoral student) for assisting in experiment and planning, and Ms. Aino Peltola (senior Laboratory Technician), for the laboratory analysis of the sample. Your precious guidance and support were extremely valuable for completing my thesis

In addition, my best regards to the Viikinmäki Wastewater treatment plant for giving me a place to perform an experiment in their vicinity. I would also like to thank Anna Kuokkanen and Laura Rossi from HSY.

During the course of field and laboratory work, I have indeed given a little time to my wife Pragya Rani Sah and my little prince Ruhaan Sah. Their creating a congenial atmosphere has gone a long way in the completion of this work.

Espoo 21.04.2019

Rajeev Sah

Table of Contents

Table of Contents.....	2
Terminology and acronyms	6
1 Introduction.....	7
1.1 Background and motivation.....	7
1.2 Objective and scope of the thesis.....	8
1.3 Overview of the thesis	9
2 Nutrients rich waste stream	9
2.1 Municipal wastewater.....	9
2.2 Characteristics of wastewater	10
2.3 Wastewater treatment: Viikinmäki WWTP.....	10
2.4 Sludge treatment	12
2.4.1 Anaerobic digestion (AD) of waste sludge.....	12
2.4.2 Principle of anaerobic digestion	12
2.4.3 Dry and wet anaerobic digestion (AD).....	13
2.4.4 Digestate	13
2.4.5 Reject water	14
3. Nutrient recovery process	14
3.1 Sedimentation theory	15
3.2 Phosphorus recovery from liquid waste	15
3.2.1 Adsorption	15
3.2.2 Chemical precipitation.....	16
3.2.3 Struvite.....	17
3.3 Nitrogen recovery from liquid waste.....	17
3.3.1 Liquid-Gas recovery of ammonia.....	17
3.3.2 Liquid – liquid recovery of ammonia	18
4. Materials and methods.....	19
4.1 Experimental study and plan	19
4.2 Sample: Reject water from Viikinmäki WWTP	22
4.3 Chemical preparation.....	22
4.4 Sampling points	24
4.5 Laboratory analysis.....	24
4.6 NPHarvest process flow design for continuous flow	25
4.7 Pre-treatment unit construction.....	26
4.8 Limekiln dust (LKD) dosing unit construction	28
4.9 Pre-treatment operation	30
4.10 Nutrient recovery operation:.....	32
5. Results	34
5.1 NPHarvest pilot and functional pre-treatment unit.....	34
5.2 Pre-treatment process.....	35
5.2.1 Chemical dose optimization and process stabilization	35
5.2.3 Pre-treatment pilot performance in different flow rate.....	36
5.2.4 Total solid in sludge liquor at optimal chemical dose	37
5.3 Comparing efficiency of limekiln dust _{ty} and limekiln dust _r	38
5.4 Ammonia recovery using Liqui-Cel 3M membrane contactor.....	39

5.5 Sludge quality analysis	40
5.6 Mass flow of nutrients and solid in NPHarvest treatment.....	41
5.7 Operational cost using NPHarvest technique	42
6. Discussion.....	43
6.1 Challenges in modifying pre-treatment from batch to continuous flow treatment process	43
6.2 What are the differences between batch process and continuous flow for NPHarvest pre-treatment technique?.....	44
6.3 Analysis of pre-treatment unit process	44
6.4 Evaluation of the NPHarvest technique.....	45
6.5 Present status and future direction of NPHarvest technology	46
7. Conclusion.....	47
References.....	48
APPENDIX	53

Table of Figure

Figure 1 Viikinmäki Wastewater Treatment Plant (HSY, n.d.).....	11
Figure 2 Process flow diagram of degradation of organic material through anaerobic digestion (Li et al., 2011).....	12
Figure 3 Schematic diagram of the rotating packed bed (RPB) system for ammonia stripping (Yuan, 2016). Components: 1:hot-plate magnetic stirrer; 2: ammonia-storage tank; 3: pump; 4: thermocouple; 5: RPB stainless steel wire mesh; 6: in situ ammonia monitor; 7: motor; 8: RPB shell; 9: air flow meter; 10: air compressor; and 11: neutralizing tank	18
Figure 4 Schematic representation of membrane contactor unit used for ammonia removal and recovery (Amaral <i>et al.</i> , 2016).....	19
Figure 5 Material and methods of the study in flow chart	20
Figure 6 Sampling points of NPHarvest treatment technique.....	24
Figure 7 Process flow design of NPHarvest technique for continuous flow	25
Figure 8 Pre-treatment with rapid mixing modification and bridge between slow mixing and settling tank.....	27
Figure 9 Constructed pre-treatment reactor. Components: 1: Settling tank; 2: Slow mixing tank; 3: LKD dosing point; 4: Rapid mixing tube; 5: Sludge liquor outlet; 6: Effluent-1 outlet; 7: Polymer dosing point; and 8: Influent-1 + Coagulant inlet	28
Figure 10 Left: Design 1 (A and B): First LKD dosing container. Middle: Design 2: modification in container and blade. Right: Design 3: Modification in outlet	30
Figure 11 Full set-up of Pre-treatment	31
Figure 12 Setup for nutrient recovery using Liqui-Cel 3M membrane contactor.....	33
Figure 13 Internal design of 3M Liqui-Cel membrane contactor.	33
Figure 14 NPHarvest technique process design for continuous flow	34
Figure 15 Various combination of chemical dose for suspended solid reduction in pre-treatment	35
Figure 16 Stabilization of effluent-1 (SS concentration) during pre-treatment	36
Figure 17 Effluent quality with optimal chemical dose with respect to influent flow rate.....	36
Figure 18 Sludge liquor total solid concentration	37
Figure 19 Average sum of Total solid (FS + VS) in sludge liquor 20-60 minute.....	37
Figure 20 (a) comparing SS concentration in effluent. (b) Comparing TS concentration by using LKD _{ty} and LKD _r	38
Figure 21 Comparing sludge liquor bed (SLB) height using LKD-r and LKD-ty.....	39
Figure 22 Liqui-Cel 3M membrane performance using feed-water.	39

Table of Table

Table 1 Pollutants in industrial wastewater (Hanchang, 2009).....	10
Table 2 Incoming wastewater properties at Viikinmäki WWTP	10
Table 3 Feedstock for wet and dry digestion	13
Table 4 Comparison of average concentration of total nitrogen in reject water in relation to the sludge treatment method (Jenicek, <i>et al.</i> , 2007)	14
Table 5 Different forms of calcium phosphate.....	16
Table 6 Overview of phosphorus recovery process from the liquid phase in municipal wastewater treatment plant (Desmidt <i>et al.</i> , 2015)	17
Table 7 List of the experimental date and order for the study	20
Table 8 Viikinmäki reject water quality from June to October 2018.....	22
Table 9 Poly-aluminium chloride physical properties	23
Table 10 Physical properties of super floc A120 polymer.....	23
Table 11 Laboratory analysis conducted by Water Laboratory, Aalto University	24
Table 12 Various chemical dose combination	35
Table 13 Nutrient and metal analysis from dry solid sample and hygiene quality (<i>E. coli</i>) in sludge liquor.....	40
Table 14 Nutrients and suspended solid mass flows	41
Table 15 Pre-treatment cost estimation (per m ³).....	42
Table 16 Nutrient recovery cost estimation (per m ³)	42

Terminology and acronyms

AD	Anaerobic digestion
Cfu	Colony forming unit
ES	Extraction solution
FS	Fixed solid
HAP	Hydroxyapatite
LKD	Limekiln dust
LW	Liquid waste
NPHarvest	Nutrient recovery
PAX	Poly-aluminum chloride
PVC	Polyvinyl chloride
RW	Reject water (liquid fraction after solid-liquid separation from digestate)
SL	Sludge liquor
SS	Suspended solid
SLB	Sludge liquor bed
TS	Total solid
VS	Volatile solid
WWTP	Waste water treatment plant
1B report	NPHarvest – technical report 2018: Nitrogen harvesting from liquid waste streams using hydrophobic gas permeable membrane.
1D report	NPHarvest –technical report 2018: Suspended solid separation.

1 Introduction

1.1 Background and motivation

Nutrient recycling has been the focus for reducing the environmental pollution and replacing the mineral fertilizers. Finland is working for finding economic value in nutrient recycling. One of the Juha Sipilä's (The prime minister of Finland, 2015) government strategic programs is to promote a circular economy (Aho *et al.*, 2015). In a circular economy, materials would circulate within the society, reduce waste and make a system with the zero loss of material. Nitrogen and phosphorus are the primary nutrients of plants. The high demand for food production has changed the path of fulfilling the plant nutrient demand with mineral fertilizers. Naturally, nitrifying bacteria and lightning fix nitrogen in the soil. The natural ways of phosphorus re-cycle are rain, through weathering cause rock release phosphate ion and other minerals and runoff end up into the ocean and incorporated into sedimentation overtimes (Vaccari, 2009). Over millions of year tectonic lift bring back phosphorus to the dry land (Vaccari, 2009). The plants take the nutrients from the soil and re-release of the nutrients back in the soil by the decomposition of organic materials. Human activity has disturbed the nutrient cycling in many ways, such as transferring huge amounts of food from the agriculture field to urban areas, replacing the natural nutrient recycling with mineral fertilizers, soil exhaustion and discharging nutrient from land to aquatic environment. Humans consume food and produce organic waste, which is collected by municipal services. These wastes are the source of plant nutrients and they need to return in agricultural soil by means of recovering nutrients from food waste or wastewater sludge. The development and technique are needed for the efficient way of recycling nutrients to fulfill the demand for food production (Aho *et al.*, 2015).

Mineral fertilizer practice has begun in the early seventeenth century. In 1908, Fritz Haber discovered the method of production ammonia-nitrogen by 'reacting atmospheric di-Nitrogen and hydrogen in the presence of iron at high pressure and temperature' (Erisman *et al.*, 2008). Later Carl Bosch developed Haber process to an industrial scale. A high amount of energy is needed to convert inactive nitrogen to active nitrogen. Phosphorus is a scarce natural element. The phosphorus component is made by using sulphur, coal and phosphate rocks. In 1680, Robert Boyle discovered urine as the source of phosphorus for plants (Driver *et al.*, 1999). In 1849, Arthur Albright began to use bones in the large commercial scale for the manufacture of phosphorus. Commercially phosphate is available from 'phosphate rock' called calcium phosphate. The rate of use of natural resources for phosphorus production is increasing which will further exploit the natural resources. The use of mineral fertilizers is predominant in modern farming due to easy application and insufficient organic fertilizer substitute (Mehta *et al.*, 2015). If we learn efficient ways of recycling, the nutrients from waste can replace some mineral fertilizers. The natural cycle of nutrients is that the plant uses nutrients to grow biomass, which is used as animal feed. The animal eats plant/plant products and produces waste which is returned to the agricultural soil. Globally the perception of waste management has transformed from liabilities to an asset.

The three main environmental issues of using mineral fertilizers are:

1. High-energy consumption.
2. Natural resources exploitation and

3. Easy leaching of the residual N and P from the field to the environment causing aquatic pollution.

Material recovery and recycling have improved waste management. Reject water (RW), which is the liquid fraction after the separation of suspended solids from the digestate. The suspended solid (SS) in reject water are mostly in the form of organic matters which remain suspended as colloid. The separation of SS from liquid waste is important as it carries pollutants and pathogens, thus it is crucial step in the wastewater treatment process (Sahu & Chaudhary, 2013). Liquid waste (LW) which is in the form of liquid and have potential harmful to environment. In modern wastewater treatment plant (WWTP), coagulation and flocculation techniques are applied in removing SS. In this process, SS form heavier flocs and are separated by gravity separation. A modified process was developed to harvest nutrients from liquid waste. The technique is called nutrient recovery technique or NPHarvest technique. This technique estimated to have high demand by LW producers such as; biogas plants, landfill site, pulp and paper industry, septic waste collector, fertilizer and food industries, waste from pig farms (Pradhan *et al.*, 2018a). Municipal WWTP has set the quality requirement for the industrial liquid waste to discharge in the sewage system (VVY, 2018). A modified technique of nutrient harvesting has tested in the batch process. This technique needed a technology development and testing on a pilot scale for industrial scale upscaling. The research and industrial area have received great interest in developing a batch into the continuous process. The batch process carries inherent limitation, which makes significant attention to the development of the continuous process in the past decade (Floudas & Lin, 2004). The continuous process over a batch process improves efficiency and reduces the cost (Floudas & Lin, 2004). However, moving a batch process to the continuous process means changing the established process, equipment and culture (Butler, 2017). The continuous process lessens the need for a large facility and decreases the waste (Butler, 2017).

The aim of this study was to construct a pilot (pre-treatment unit) for NPHarvest process which can removes phosphorus and SS from liquid waste. The pre-treated water was then used in nutrient recovery step for nitrogen harvesting, which was another aim for this project.

1.2 Objective and scope of the thesis

1. Design a continuous-flow pre-treatment process based on previous batch process tests.
2. Construct a pilot plant based on the design.
3. Process optimization considering flow rate, chemical dosing and sludge liquor solid content.
4. Testing Liqui-Cel 3M membrane contactor for nitrogen recovery.

NPHarvest technique was designed to treat various types of liquid waste. The scope of the thesis will be limited to use only Viikinmäki reject water. The sludge liquor (SL) produced in pre-treatment needs further processing, but this sludge liquor treatment is not studied in this thesis.

This work on NPHarvest pilot development will answer following questions.

Process development

1. What are the challenges of modifying pre-treatment from batch to continuous flow treatment process?
2. Is the pre-treatment from batch to continuous process feasible?
3. Could lime kiln dust possibly be dosed continuously as a solution?

Technology feasibility study

4. How efficiently liquid waste can be treated with NPHarvest technique?
5. Is it economically feasible to upscale from pilot to industrial scale?

1.3 Overview of the thesis

This study started with familiarization with previous research done by NPHarvest group. The NPHarvest research group has developed a modified technique to treat liquid waste and all the experiments have been performed in the Water Laboratory of Aalto University. Chapter 1 presents the background, need of research and motivation. Chapters 2 and 3 contain a literature study. They contain the municipal wastewater and treatment process. The second part of the literature study focuses on nutrient removal and recovery. Sedimentation theory was also included because it is the predominant part of the pretreatment and necessary for understanding the process. Chapter 4 explains the materials and the method used for my study. The material used was NPHarvest technique process design and construction of the pre-treatment pilot. The experimental design was used for pre-treatment and nutrient recovery operation was methods of study. Chapter 5 contains the results from design, construction, the chemical dose optimization of pre-treatment and performance study of nitrogen recovery using Liqui-Cel 3M membrane contactor. This chapter also includes comparing the efficiency of LKD_{ty} and LKD_r , sludge liquor quality analysis, mass flow of nutrients and solid and operation cost in NPHarvest process. Chapter 6 covers the discussion about challenges, differences between batch and continuous process, feasibility and present status and future direction of NPHarvest technology. Chapter 7 contains the conclusion of the work.

2 Nutrients rich waste stream

2.1 Municipal wastewater

The municipal sewage contains both, wastewater from domestic sources and industries. Finnish Water Utilities Association has defined that ‘domestic wastewater refers to the wastewater generated by human metabolism and household operation’ (VVY, 2018). Domestic wastewater includes waste from washing, bathing and flushing toilets from the residence, business building and institutions. Wastewaters from manufacturing plants have pollutants as bio-waste, metals, organic chemicals, organic micropollutants, oils, and chemicals. Other than industrial wastewater some commercial operators also create wastewater such as wastewater resulting from car washing and servicing operation, landfill leachate, wastewater from the treatments of contaminated soils, wastewater from laboratories, laundries, dental care and hospital (VVY, 2018). Municipal wastewater is liquid waste collected in sanitary sewers. Several cities have at least partly the combined sewer system where storm water and sanitary wastewater are collected together in same pipe network. Table 1 has listed the types of industries and pollutants produced from them.

Table 1 Pollutants in industrial wastewater (Hanchang, 2009)

Types of Industry	Pollutants
Iron and Steel	BOD, COD, oil, metals, acids, phenols and cyanide
Textiles and Leather	BOD, solid, sulphate and chromium
Pulp and paper	BOD, COD, solids, chlorinated organic compounds
Petrochemicals and refineries	BOD, COD, Minerals oils, phenols and chromium
Chemicals	COD, organic chemicals, heavy metals, SS and cyanide
Non-ferrous metals	Fluorine and SS
Microelectronics	COD and Organic chemicals
Mining	SS, metals, acids and salts

In Finland, it is recommended that industrial wastewater conducted to the municipal sewage network follow the requirements stated in the ‘Finnish industrial wastewater guide’ (VVY, 2018). The guide considers the information on types of industrial wastewater, instruction for preparing an industrial wastewater agreement, the formula of the increased fee, monitoring of industrial wastewater and practical example of functional solution.

2.2 Characteristics of wastewater

The municipal wastewater liquid fraction (99.9 %) is water and the small concentration of solid fractions (organic and inorganic solids). The organic matters present in municipal wastewater are carbohydrate, fats and proteins. The wastewater also contains a small portion of toxic elements such as organic micropollutants (antibiotics, hormones, and pesticides), arsenic, chromium, cadmium, copper lead, mercury, zinc. Table 2 lists the constituents of incoming wastewater at Viikinmäki. It helps in comparing the quality of the reject water after anaerobic digestion of activated sludge at Viikinmäki WWTP.

Table 2 Incoming wastewater properties at Viikinmäki WWTP

Constituents (mg/l)	Low Strength	High Strength
Total solid (TS)	390	1230
Volatile solid (VS)	270	860
Suspended solid (SS)	120	580
Total Nitrogen	20	75
Total Phosphorus	2.2	9.6

The characteristics of wastewater differ depending upon the type of industries and lifestyle of the city.

2.3 Wastewater treatment: Viikinmäki WWTP

Viikinmäki central treatment plant was built in 1986 and completed in 1994. It receives an average of 100 million cubic meters of wastewater annually from the Helsinki metropolitan region. Around eighty-five percent of wastewater is coming from domestic and fifteen percent come from industrial waste. Viikinmäki is the largest WWTP in Nordic countries. The treatment process is quite efficient which shows, 95% of phosphorus and 90 % of nitrogen removal from wastewater (HSY, n.d.). Figure 1 presents the wastewater treatment process unit of Viikinmäki WWTP.

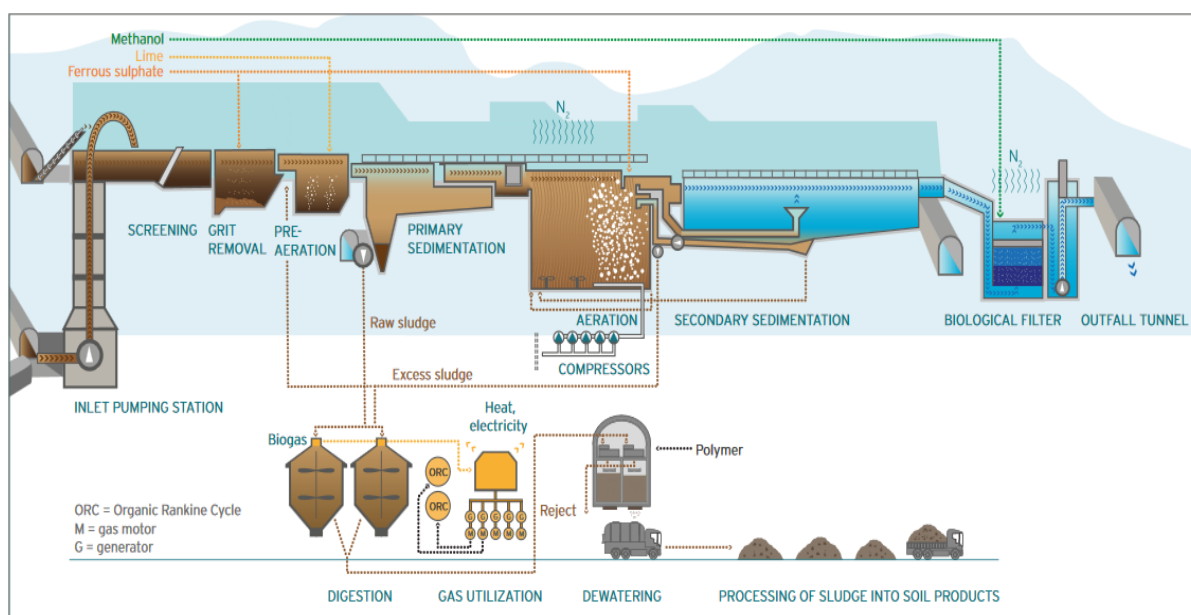


Figure 1 Viikinmäki Wastewater Treatment Plant (HSY, n.d.)

The Viikinmäki WWTP have the following steps in the treatment process: screening, grit and grease removal, primary settling, activated sludge process, biological denitrifying post-filter and discharge (Tomperi *et al.*, 2017). Grit removal includes sand, gravel, other heavier materials, and larger organic particles such as food waste. Grease and oils are lighter than water, which floats on the surface, and can be scraped from the surface of the tank. The phosphorus removal is carried out by precipitation. Ferrous sulphate is used as precipitant where phosphorus is bound with sludge. In the needed case, Calcium hydroxide is used in the aeration tank to increase the alkalinity of water where nitrification consumes alkalinity. In primary settling tank easily settling materials are separated from water. Activated sludge processes have biological treatment and secondary sedimentation. Biological treatments have nitrification and denitrification after primary sedimentation. Activated sludge containing organic matter and nutrients are separated in the secondary sedimentation tank. After the secondary sedimentation tank, wastewater passes into the biological filter where enhanced denitrification from wastewater takes place. Excess activated sludge from the secondary settler and sludge from the primary settler further processed in the digester.

The digester receives raw sludge from the treatment process and liquid waste from outside (i.e. fats and industrial sludge). The digestion process occurs in a mesophilic condition where the temperature is 30-38 °C and retention time is 14-17 days. Viikinmäki have four digestion tanks which capacity is 10 000 m³ each. The daily Sludge inflow for the digestion ranges from 2 400 – 2 900 m³. The by-product of digestion is digestate. Digestate is further separated into a solid and liquid part. This liquid part has named as reject water. NPHarvest technique was applied to treat RW after anaerobic digestion. The characteristics of Viikinmäki reject water are presented in Chapter 4.7.

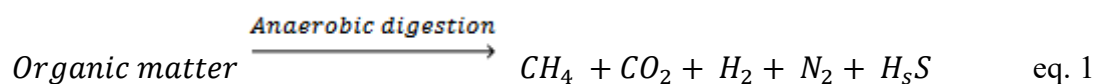
2.4 Sludge treatment

2.4.1 Anaerobic digestion (AD) of waste sludge

This treatment method is widely applied in treating the organic sludge in waste treatment plants. Anaerobic digestion reduces the amount of sludge volume and produces methane which can be utilized in combined heat and power production (Takiguchi *et al.*, 2004). The sludge received from a primary and secondary sedimentary tank of WWTP contains a high amount of organic matters, which needs to be further treated in anaerobic digestion. The anaerobic bacteria break down the organic matter into carbon dioxide (CO₂) and methane (CH₄). The digested sludge is dewatered, where solid part (digestate) and liquid part (rejected water) need further treatment. Reject water from sludge digestion contains higher than 1000 mg/L ammonium nitrogen as well as a high level of phosphorus (Arnold *et al.*, 2000).

2.4.2 Principle of anaerobic digestion

Anaerobic digestion (AD) converts the carbonaceous contents of the sludge to gaseous methane, carbon dioxide and hydrogen, hydrogen sulphide and nitrogen as gas (eq. 1). This is the most likely employed treatment process of the sludge. This process has accomplished in the absence of oxygen.



The process produce mixture of gases in which methane gas is 55-75% and CO₂ are 25-45% (De Mes *et al.*, 2003). The rest of the gases are H₂, N₂, and H₂S in very small amount. The digestate residual have chemically stable organic matter and contains small amount of pathogen (Nazaroff & Alvarez-Cohen, 2001). Figure 2 shows how the organic matter degrades during anaerobic digestion.

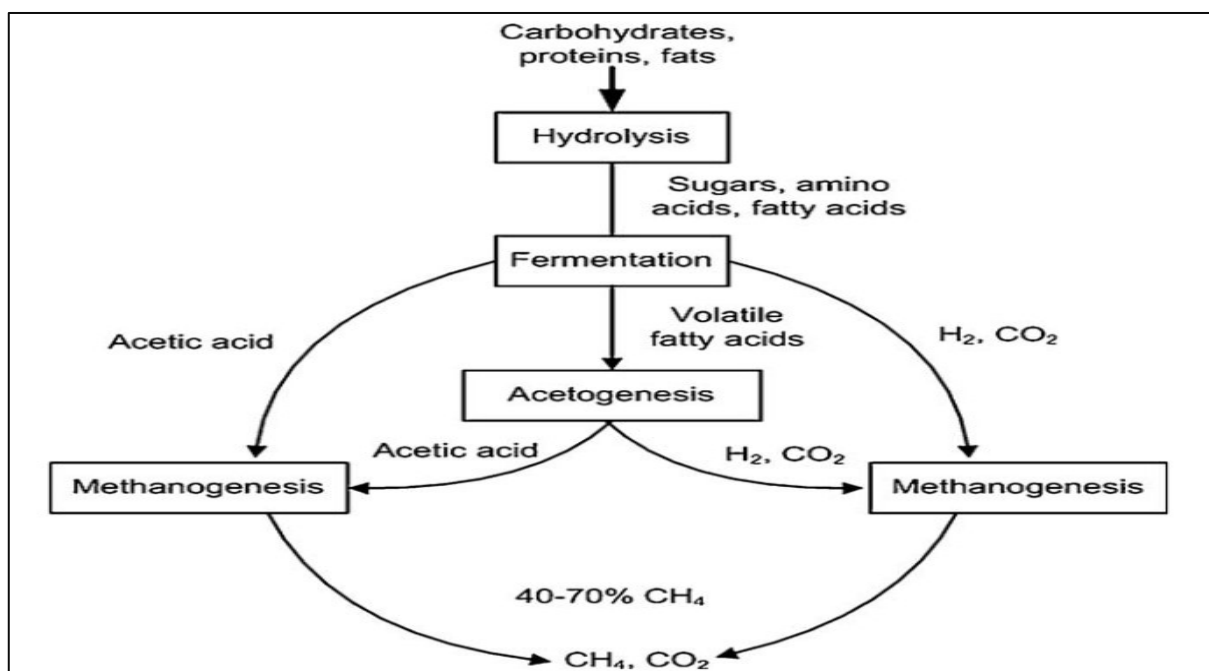


Figure 2 Process flow diagram of degradation of organic material through anaerobic digestion (Li *et al.*, 2011)

AD occurs itself in the nature. Microbes need suitable environment to start decomposing organic matter. The digestion process often seen at the bottom of the lakes, in swamps, peat bogs and landfills (Braber and Novem, 1995). The anaerobic digestion followed by four different microorganisms with the following steps: hydrolysis, fermentative, acetogenic and methanogenic. The digestion process depends on the environmental condition such as the temperature, humidity, microbial activity and waste properties (Braber and Novem, 1995). AD can perform either the batch or continuous process. Depending on the solid concentration of waste sludge, anaerobic digestion is divided into wet and dry digestion. The end-product of anaerobic digestion is digestate.

2.4.3 Dry and wet anaerobic digestion (AD)

The dry and wet AD differentiate depending on the solid concentration of organic waste. In wet AD process, the dry solid content ranges from 10 – 15 % whereas in dry AD process, the dry solid contents of 20-40 % of dry matter (Luning *et al.*, 2003). Municipal sewage sludge, animal manure and food wastes are generally treated as wet digestion. Organic waste from municipal solid waste, lignocellulose biomass as crop residues and energy crop are treated as dry digestion. Dry digestion is considered as advantageous over wet digestion because of smaller reactor volume, because of low water content then wet digestion less energy consumption for heating and higher retention of biomass (Li *et al.*, 2011). Table 3 shows the feedstock characteristics of dry and wet digestion.

Table 3 Feedstock for wet and dry digestion

Quantity	Wet digestion	Dry digestion
Water content of the feedstock	>85 %	<80%
Total solids destroyed	40 – 60 %	Depending on the lignin content
Destruction of volatile solids waste	60 – 80 %	90 – 98 %
Biogas production per kg of volatile solids destroyed	0.5 – 0.75 m ³ /kg	0.625 – 1 m ³ /kg
Temperature (mesophilic)	30 – 38 °C	30 – 38 °C
Temperature (thermophilic)	55 – 60 °C	55 – 60 °C

The methane gas production depends on the digestibility of organic matter, bacteria culture, sludge retention time and temperature (Tchobanoglous, 1993).

2.4.4 Digestate

The anaerobic digestion process produces < 1 % solid content liquid by-product, which is known as digestate. The water content of the digestate ranges from 75-96% depending upon digestion technique and feed material (Christensen, 2011). It consists of the mineralized remains of dead and living biomass. Acidogenesis digestate contains a large amount of lignin and cellulose and dead bacterial cells. This digestate used for low-grade building products such as fibreboard. Methanogens digestate is rich in nutrient and is used as fertilizer. The source of waste stream dictates the need for testing the potential of toxic element in digestate. The post-treatment of digestate is considered by the end user, further dewatering treatment or aerobic digestion (composting/stabilization) (Akunna, 2015).

2.4.5 Reject water

The liquid fraction of dewatered digestate after anaerobic digestion of waste sludge is known as reject water. The recycle of reject water in Municipal WWTP can contribute up to 80 % of nitrogen and phosphorus load (Guo *et al.*, 2010). Bachmann *et al.*, (2016) has estimated 7-20 % of nitrogen remains in the solid fraction of dewatered digestate and the remaining 80% in reject water. Reject water generated in wastewater treatment plant is about 2% of the influent flow of WWTP (Janus & Roset, 1997). The reject water by recirculating in influent add significant amount of nitrogen load (Volcker *et al.*, 2006). The high loads of nitrogen decrease the efficiency of biological treatment and consume more energy and resource to remove nitrogen. The high concentration of nutrient and organic load needs to remove before recirculating into the mainstream of WWTP (Pitman, 1999) to increase the efficiency of WWTP. Bachmann *et al.*, (2016) has reported that ‘organic phosphorus in digestate probably has a very small particle size and remain in the liquid fraction’. Table 4 shows the total nitrogen concentration in waste sludge and digested sludge.

Table 4 Comparison of average concentration of total nitrogen in reject water in relation to the sludge treatment method (Jenicek, *et al.*, 2007)

Method of Sludge Management	N-total (mg/l)
Waste activated sludge without stabilization	20 – 40
Mixture of waste activated and primary sludge without stabilization	50 – 100
Separated aerobic digestion	50 – 300 (700) *
Mesophilic anaerobic digestion	500 – 1000
Thermophilic anaerobic digestion	900 - 1800

*Autothermal aerobic digestion

A well-known technique, biological treatment is also applicable to remove nitrogen from reject water. Anaerobic heterotrophic denitrifying bacteria need inorganic carbon as foods are provided by addition of external electron donor such as acetate, methanol or ethanol (Guo *et al.*, 2010). A major form of phosphorus removal was achieved by chemical precipitation. Few studies on different types of the method applied in nutrient removal and recovery technology have been explained in the subsections of Chapter 3.

3. Nutrient recovery process

Recovery: Recovery is defined as the recapturing nutrient as chemical compound or in pure form. In NPHarvest technique ammonium is recovered as ammonium sulphate. So, process is regarded as recovery.

Removal: Removal is defined as separating or taking out from system. In pre-treatment process, sludge liquor still needs further processing to accept recycle product. So, here in my thesis, I regard it as removal.

Loss: Escaping out to the air as gas form.

3.1 Sedimentation theory

In order to treat wastewater to be discharged in the environment, it is important to remove variously dissolved and suspended particles. These particles may include heavy metals, oil, grease, and organic materials. Removal of these contaminants typically is done by a combination of chemical reaction and physical separation to remove solid forms from the liquid. In a wastewater treatment plant, sedimentation (settling) is applied widely in solid separation. Sedimentation is the separation of the particle based on the gravitational force from the differences in density between particles and the fluid. Stokes law states larger particles settle much faster than smaller ones. Every particle has some weight and when it falls through a fluid, it accelerates until it reaches a constant terminal velocity. Terminal velocity of an object can determine by knowing density of the fluid, density of the body, viscosity of the fluid, the shape and orientation of the body. In NPHarvest technique, pre-treatment include coagulation, flocculation, and ballasted sediment. Hunt (1982) and Morel and Schiff (1990) 'have derived a simplified solution for mass removal of solids by second-order dependency on mass concentration' (Farley & Morel, 1986).

$$\frac{dC}{dt} = -BC^2 \quad \text{eq. 2}$$

Coagulation and sedimentation occur simultaneously to describe sedimentation kinetics. Sedimentation process depends on the coagulation and size of flocs formation. Smaller particles have zero settling velocity, but coagulation help in neutralizing the solution and small-suspended particle capable of sticking together and flocculation is gently mixing stage where particle grow in micro floc. The particle size grows bigger in flocculation process and critical volume size of particle settle infinitely fast (Kevin *et al.*, 1986). The polymer is a coagulant aid, which act as to bridge and bind the floc. This process makes the flocs heavier and increase settling rate. The density of floc particles can be increased by applying a ballasting agent such as micro sand or fine sand. The ballasted floc-settling rate increases faster than floc without ballasting aid (Sedimentation Process, n.d.).

3.2 Phosphorus recovery from liquid waste

3.2.1 Adsorption

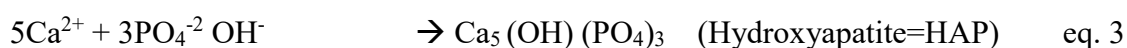
Adsorption is a surface phenomenon of accumulation of higher concentration of molecular species on the surface of sorbent. Adsorption technology is regarded as successful and widely applied in the field of wastewater treatment process (Dong *et al.*, 2012). Phosphate removal by adsorption method is one of the convenient methods because of simple and low-cost operation and design (Loganathan *et al.*, 2014). Once the sorbent is saturated, it can be used directly as a source of phosphorus or regenerated sorbent by precipitation-sorbet phosphate. The adsorption and desorption are dependent upon physical and chemical characteristics of the sorbent (Loganathan *et al.*, 2014).

Tu *et al.*, (2016) has studied La-modified natural clinoptilolite for phosphorus removal from the wastewater. The result observed by modified clinoptilolite was 98.38% phosphorus removal from real wastewater. This method is applicable for separating different forms of phosphorus from wastewater and give more value because of high efficiency, low cost, and

possible to harvest different form of phosphorus (Tu *et al.*, 2016). The adsorption/Ion exchange technology also give high phosphorus recovery rate and treated effluent can have phosphorus concentration <0.1 mg PO₄-P /l (Mehta *et al.*, 2015). They have stated that ion exchange technology is suitable for suspended solid concentration up to 2000 mg/l with low solid content (<2000 mg/L). This technology has been also regarded as hybrid nutrient accumulation-nutrient where nutrient adsorbed on the sorbent media can directly be used as agriculture fertilizer (Mehta *et al.*, 2015).

3.2.2 Chemical precipitation

The widely preferred recovery of phosphorus from the liquid phase is precipitation and crystallization (Chen *et al.*, 2009). The phosphorus recovery can be applied at any stage of biological treatment and the efficiency can be increased by choosing appropriate chemical dose and environment (Ye *et al.*, 2017). The other most commonly used precipitants are calcium and magnesium, which can react with phosphorus and form hydroxyapatite and struvite respectively (Ye *et al.*, 2017). The respective chemical reaction is shown in eq. 3 and 4. The formation of struvite and HAP can only occur when the concentration of magnesium/calcium, ammonia and phosphorus are in the right proportion (Ye *et al.*, 2017).



With the above precipitation approach, struvite can directly be used as fertilizer, but hydroxyapatite is sent to the phosphate industry for recycling (Ye *et al.*, 2017). Petzet *et al.*, (2012) found that iron and aluminium salt precipitation is prohibited because of not suitable as fertilizer. Ye *et al.*, (2017) has reported that the strong bond with phosphate makes the release as mineral phosphate difficult. The chemical precipitation involves various factors such as ion concentration, ion strength, temperature, ion type and pH (Desmidt *et al.*, 2015). The pH adjustment plays an important role to achieve high yield and purity and to minimize free ammonium and carbonate influence (Bi *et al.*, 2014). The pH > 8 helps in the formation of struvite and HAP but pH > 10 reduce phosphate recovery efficiency (Ye *et al.*, 2017). The recovered calcium phosphate is widely accepted by the phosphate industry because it is a good replacement of phosphate rock (Driver *et al.*, 1999). The drawback of lime for phosphorus precipitation is a large amount of lime is required to elevate pH since precipitation of calcium phosphate is less independent of phosphorus concentration (Desmidt *et al.*, 2015). The different forms of calcium phosphate precipitates are presented in Table 5.

Table 5 Different forms of calcium phosphate

Name	Formula
Dicalcium phosphate dehydrate (DCPD)	CaHPO ₄ ·2H ₂ O
Dicalcium phosphate anhydrous (DCPA)	CaHPO ₄
Octacalcium phosphate (OCP)	Ca ₈ H(PO ₄) ₆ ·5H ₂ O
Tricalcium phosphate (TCP)	Ca ₃ (PO ₄) ₂
Amorphous calcium phosphate (ACP)	Ca ₃ (PO ₄) ₂
Hydroxyapatite (HAP)	Ca ₁₀ (PO ₄) ₆ (OH) ₂

3.2.3 Struvite

The struvite formation in the wastewater treatment plant is achieved by pH, magnesium concentration and retention time (Desmidt *et al.*, 2015). The theoretical molar ratio of Mg: N: P are 1:1:1 for the formation of struvite. The struvite precipitation during anaerobic digestion has major problem with clogging of pipe (Cieřlik *et al.*, 2016).

Table 6 Overview of phosphorus recovery process from the liquid phase in municipal wastewater treatment plant (Desmidt *et al.*, 2015)

Full Scale process	Influent type	Chemical	Recovered Product	Recovery efficiency
ANPHOS	Anaerobic digestion effluent	MgO	Struvite	80 – 90
PHOSPAQ	Anaerobic digestion effluent	MgO	Struvite	80
NuReSys	Anaerobic digestion effluent	MgCl ₂ , NaOH	Struvite Biostru	85
Phosnix	Anaerobic digestion effluent	NaOH, Mg (OH) ₂	Struvite	90
Ostra Pearl	Anaerobic digestion effluent	Sand, NaOH, H ₂ SO ₄ , Ca (OH) ₂	Struvite crystal green	85
Airprex	Anaerobic digestion effluent	MgCl ₂ , Flocculent	Struvite	80 - 90

In wastewater treatment, process magnesium is a limiting factor for the formation of struvite. Magnesium chloride or magnesium oxide is added for struvite formation. The experimental dose of magnesium is higher than the theoretical value because magnesium also reacts with soluble oxygen and some organic substances (Ye *et al.*, 2017). The high concentration of ammonium in the wastewater is significant to the formation of struvite by contributing pH buffering effect and secondly nitrogen supplier (Ye *et al.*, 2017).

3.3 Nitrogen recovery from liquid waste

3.3.1 Liquid-Gas recovery of ammonia

This process is widely used to remove and recover ammonia from various type of ammonia-rich water (Yuan, 2016). The ammonia removing from ammonia rich liquid require mainly temperature, pH control (Yuan, 2016) and air flow (Zhang, 2012). The operation process is unaffected with wastewater quality and ammonia concentration. The process involves the physiochemical process where transferring the ammonium from wastewater into the gas phase and then gas ammonia is reacted with an acid solution to form an ammonium sulphate, which is used as mineral fertilizer. Figure 3 shows the rotating packed bed (RPB) system for ammonia recovery.

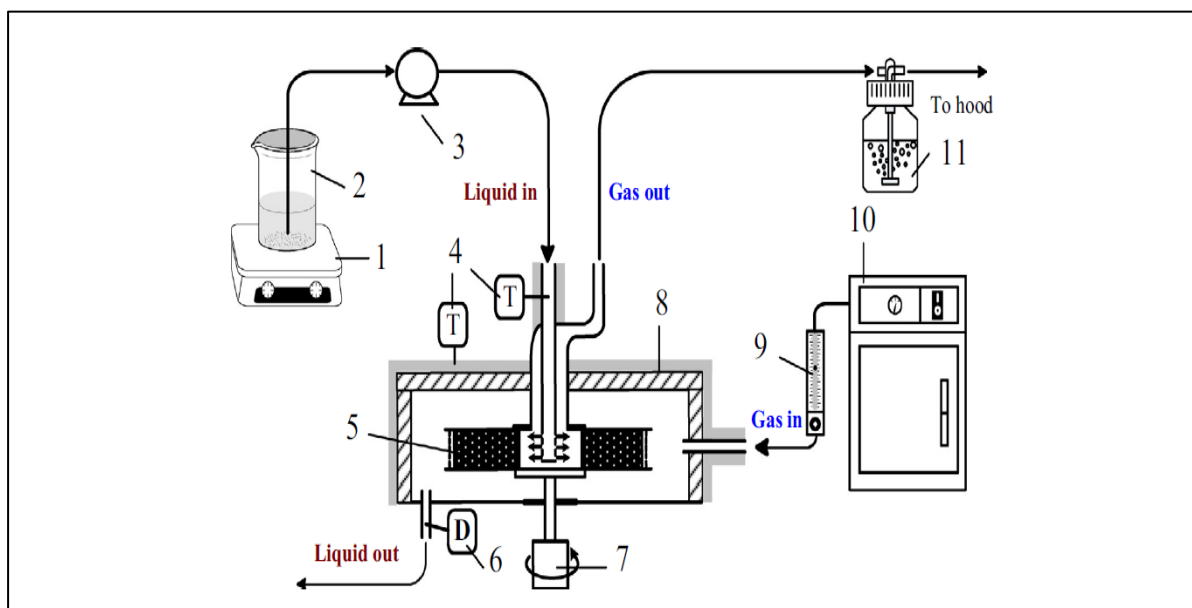


Figure 3 Schematic diagram of the rotating packed bed (RPB) system for ammonia stripping (Yuan, 2016). Components: 1: hot-plate magnetic stirrer; 2: ammonia-storage tank; 3: pump; 4: thermocouple; 5: RPB stainless steel wire mesh; 6: in situ ammonia monitor; 7: motor; 8: RPB shell; 9: air flow meter; 10: air compressor; and 11: neutralizing tank

Yuan, (2016) has tested with 1000 mg/L ammonia concentration in wastewater by using continuous-flow rotating packed bed at a temperature from 25 to 40 °C. The ammonia concentration in effluent was measured 16 mg NH₄-N/l at 25 °C by a series of four stage rotating packed bed and 6.8 mg NH₄-N /l at 40 °C by a series of three stage rotating packed bed. The drawback of liquid-gas stripping is of high cost operating per unit volume, need for pre-treatment of feed-water and production of high pH wastewater that is not suitable for WWTP (Mehta *et al.*, 2015).

3.3.2 Liquid – liquid recovery of ammonia

This technique has applied Gas permeable membrane technology to recover ammonia from liquid waste to extraction solution. Acid solution used for recovering nitrogen from liquid waste is named as extraction solution (ES). Membrane technology has become more popular in the last decade because of low chemical additives, simple in operation and relatively low energy consumption (Kang *et al.*, 2014). Vanotti *et al.*, (2011) had tested 140 to 1400 mg/l NH₄-N and found that the rate of nitrogen recovery by gas permeable membrane was higher with higher ammonia concentration in swine manure. The rate of ammonia diffusion through the membrane also depends on the pH of wastewater (Amaral, 2016). This process is not suitable for containing hydrophobic compounds such as fats, oils, and grease, as it blocks the membrane pore and fouling (Mehta *et al.*, 2015). Amaral *et al.*, (2016) made a study on ammonia removal and recovery from landfill leachate using membrane contactor. Figure 4 is a schematic representation of ammonia removal and recovery by using membrane contactor.

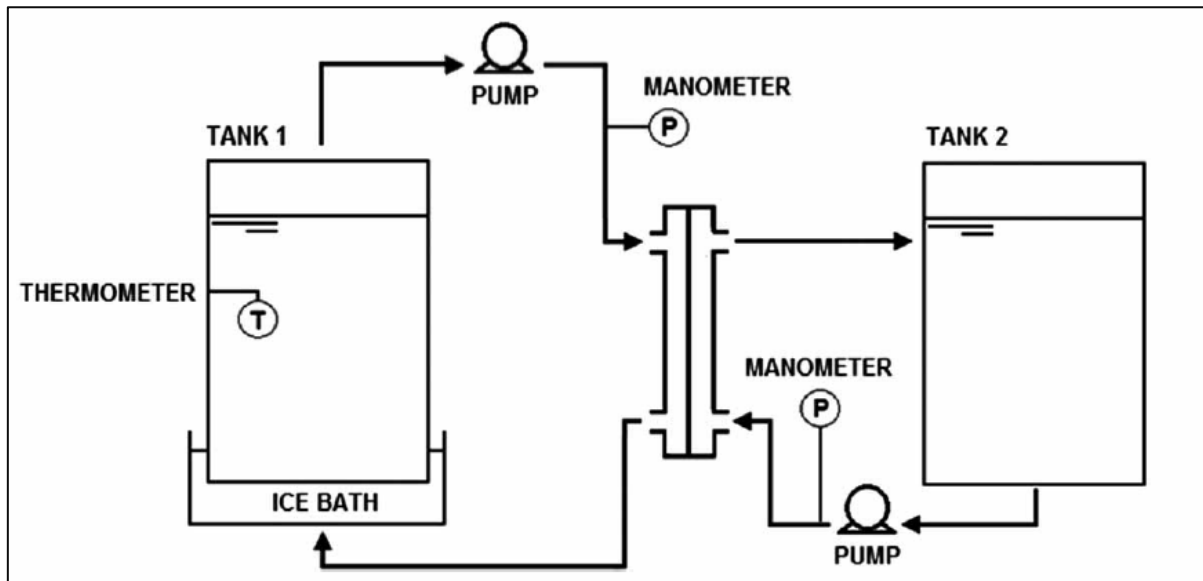


Figure 4 Schematic representation of membrane contactor unit used for ammonia removal and recovery (Amaral *et al.*, 2016)

Tank-1 has landfill leachate and tank-2 has an ES as sulphuric acid. Both liquids were recirculated during experiment. Membrane contactor has a hydrophobic membrane which, separates the two liquid from mixing. Both liquids circulated in counter current flow direction. Amaral *et al.*, (2016) has presented that 99.9% ammonia removed with 79% of ammonia recovery using membrane contactor. This treatment needs a pre-membrane filtration of liquid waste to use as the influent in the operation.

4. Materials and methods

4.1 Experimental study and plan

The study period for this thesis was from March 2018 until the end of August 2018. The experimental study was extended for two months due to delay in pilot construction and membrane availability. Most of the time was used in constructing and testing the pre-treatment pilot. Nutrient recovery pilot was not constructed during this study due to unavailability of the proper membrane. The testing for nutrient recovery in this thesis was done with Liqui-Cel 3M membrane contactor. The pre-treatment pilot was assembled and tested in the Viikinmäki wastewater treatment plant. Figure 5 illustrating how the work was planned and completed and bold and black text shows my own contribution of the study. Table 7 listed the experimental time and order of study.

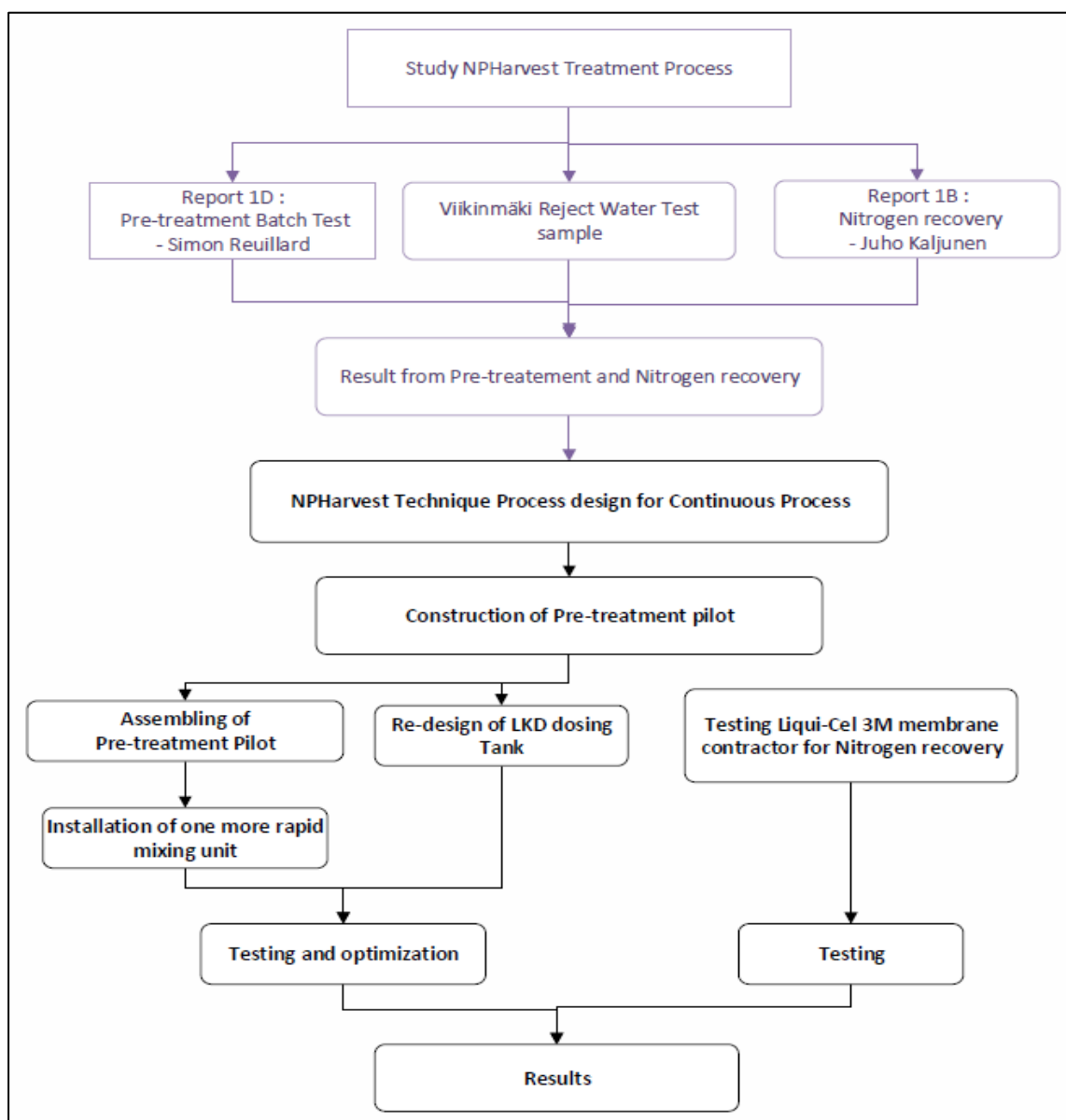


Figure 5 Material and methods of the study in flow chart

Table 7 List of the experimental date and order for the study

Work	Date	Remarks
Literature and previous work study	01.03 – 15.05.2018	Collected information for literature work and studied previous work done by NPHarvest researchers.
Pre-treatment reactor	16.05 – 01.06.2018	Constructed and assembled pre-treatment units (Rapid mixing, slow mixing and settling tank)
Tested pre-treatment reactor	01.06	At Aalto water laboratory
Pre-treatment reactor	06.06	Delivered and setup in Viikinmäki WWTP
Started work at Viikinmäki	07 - 08.06.2018	Demonstrated pre-treatment reactor for European phosphorus conference 2018

Pre-treatment experiment chemical dosing based on batch test with influent flow rate 100 l/hr	14 – 15.06.2018	Difficulties in achieving ballast sediment
Batch experiment at Viikinmäki	19 – 20.06.2018	Testing chemical performance
Experiment with influent flow rate 60 l/hr	22 – 25.06.2018	Because of difficulties in achieving ballast sediment. I decided to decrease the influent flow rate to increase retention time. Problem with LKD dosing
Modified the pre-treatment reactor by installing one more rapid mixing	28 – 29.06.2018	Reducing influent flow and installing new rapid mixing for LKD help in mixing but does not improve the treatment process.
Experiment with freshly prepared chemical	02 -03.07.2018	Improvement in the treatment process and realize polymer solution I had was wrong.
Experiment with different chemical dose	03 – 06.07.2018	First-time sample delivered to the water lab for analysis. LKD-ty dosing problem due to clogging.
Changed in LKD dosing bucket	08 – 09.08.2018	Sifting outlet from bottom to 10 cm up. Still clogging issue remain which disturbs while making a long run.
Experiment to optimize influent flow and chemical dosing	15 – 17.08.2018	Some issue with LKD-ty dosing but succeeded to make a sample and delivered to water laboratory.
Preparing new LKD dosing tank	03 - 05.09.2018	Tested in water laboratory before delivery to Viikinmäki. The issue was dosing concentration increases with time. LKD-ty over and now LKD-r was used for experiment. I don't know the difference of LKD-ty and LKD-r
Modified LKD tank	13 - 14.09.2018	Overnight testing LKD-r dosing. Succeeded in making constant LKD dosing tank.
Modified LKD dosing tank delivered to Viikinmäki	21.09.2018	Pre-treatment reactor needs to be below LKD dosing tank to avoid clogging.
Long run test of pre-treatment unit	27 – 28.09.2018	Pre-treatment developed for a continuous process. Still, we need to learn on controlling effluent-1/ sludge liquor outflow ratio.

Testing Liqui-Cel 3M	26.09 and 01 – 02.10.2018	Effluent sample from pre-treatment membrane contactor in water brought to water laboratory
Testing LKD-ty and LKD-r	04.10.2018	Testing effluent quality and sludge liquor settling rate.
Dry sludge prepared	08 – 09.10.2018	Sample sent to Aalto chemistry laboratory for metal analysis.
Effluent and sludge liquor for hygiene quality analysis	15.10.2018	<i>E.coli</i> count from the sample.
Laboratory test of samples	15.08 – 15.10.2018	Result analysis
Thesis	02.09.2018–30.01.2019	Writing

4.2 Sample: Reject water from Viikinmäki WWTP

In Viikinmäki WWTP, digestate is proceeds to dewater by centrifugation. Cationic polymer (polyacrylamide) is added to improve dewatering. Dewatered digestate content up to 30% of total solid. The rejects water (liquid fraction of dewatered digestate) goes through two-hour settler tank. This reject water from settler tank was used as influent for our NPHarvest pilot plant. Currently, Viikinmäki reject-water is recirculating to the main treatment process, which is 0.7 - 1 percentage of influent flow. The hydraulic changes are quite small due to reject-water recirculation, but total nitrogen concentration increased by 17% and total phosphorus by 1.7%. Viikinmäki reject water characteristics presented in Table 8 are low, high and average concentration taken from process monitoring samples measurements of Viikinmäki wastewater treatment plant.

Table 8 Viikinmäki reject water quality from June to October 2018

Constituents (mg/l)	Low Strength	High Strength	Average
Suspended solid	550	2225	1116
Total Phosphorus	8	26	14
Orthophosphate (PO ₄ -P)	0.53	1.98	1.20
Total Nitrogen	791	1072	909
Ammonium (NH ₄ ⁺ -N)	636	801	723
pH	7.9	8.1	8

4.3 Chemical preparation

There were three different chemicals used in pre-treatment process. All chemicals were dosed as percentage solution and it was prepared using reverse osmosis water. Chemicals preparation was as follows:

a) Poly-aluminium chloride (PAX XL100) Coagulant

The coagulant (PAX XL100) 10% v/v solution was used for this study. The chemical was prepared by mixing 71.4 ml coagulant in reverse osmosis water and making final volume one litre result 10% v/v solution. During experiment, I also used 15 and 20% solution because of

the pump pumping capacity (maximum capacity: 20-22 ml/min). Table 9 presents the physical properties of coagulant.

Table 9 Poly-aluminium chloride physical properties

Physical Properties	
pH	<1
Density	1.36-1.42 g/cm ³
Viscosity	30-50 Millipascal Second
Aluminium (Al ³⁺)	9.30 %

b) Super flocc A-120 polymer

The chemical was dosed in aqueous form. Polymer took 30-40 min to dissolve in water with the help of high-speed magnetic stirrer. The polymer above 0.5% solution is highly viscous which is difficult to pump. I used 0.01% w/v polymer solution. The chemical was prepared by dissolving 0.1 g polymer in one litre reverse osmosis water. Table 10 presents physical properties of polymer.

Table 10 Physical properties of super flocc A120 polymer

Physical properties	
Appearance	White, granular powder
Degree of Charge, (mole %)	20
Relative molecular weight	High
Bulk density. kg/m ³	825+/-50
pH of 0.5% solution	5 - 7
Viscosity, cps	
0.10%	200
0.25%	400
0.50%	800

The chemical nature is anionic polyacrylamide. ‘According to EU directive 67/548/EEC or 1999/45/EC, it is not a hazardous substance. The solution become slippery when dissolved in water. It contains no components considered both persistent, bio accumulative and toxic, or very persistent and very bio accumulative at level of 0.1% or higher’ (Kemira, 2016).

c) Lime kiln dust

Lime kiln dust (LKD) is also called as structure lime. It is white powder granules (particle size: 100% <0.25 mm and 50 % < 0.032 mm), which contain 80 % calcium carbonate and 20 % calcium oxide. LKD dosed as an aqueous solution of 10-20% v/v solution. Percentage solution was prepared based on pump capacity. I used up to 20 % v/v solution of LKD and it works perfectly. Equation 6 was used to calculate the volume of LKD when powder LKD dissolved in water. It was used to prepare the V/V based percentage solution. Nordkalk was associated with NPHarvest project and supplied LKD for this research project. During my experiment, I received LKD in two lots. LKD-ty was from Tytyri (Lohja) plant and LKD-r was from Raahe plant. Both plants are in Finland.

Porosity of LKD = 0.6 or 60 % (calculated from experiment)

$$P = \frac{V-d}{V} \quad \text{eq. 5}$$

$$d = V - (P * V) \quad \text{eq. 6}$$

P = porosity, V = volume of LKD, d = displacement of water

Note: weight of LKD is same in volume measurement (i.e. 10 g = 10 ml).

4.4 Sampling points

The first part of NPHarvest technique was pre-treatment. The sampling points for the pre-treatment process were 1 - 3 shown in Figure 13. Nutrient recovery was the second part of NPHarvest technique. Ammonia recovery efficiency was analysed by making samples at 4 - 6.

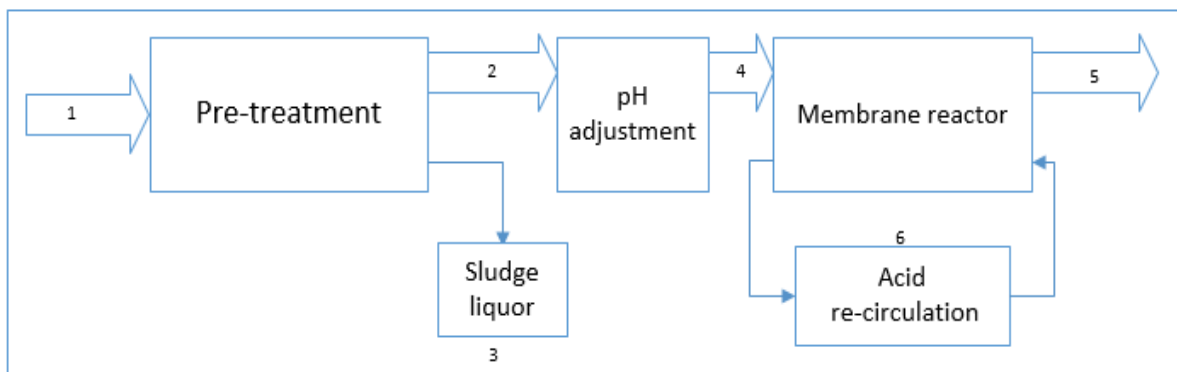


Figure 6 Sampling points of NPHarvest treatment technique

Sampling points:

1. Reject water (Influent-1)
2. Pre-treated water (Effluent-1)
3. Sludge liquor (SL)
4. Feed-water (influent-2)
5. Effluent-2
6. Extraction solution (ES)

4.5 Laboratory analysis

Table 11 presents the laboratory analysis conducted at Aalto University Water laboratory. The samples were collected during pre-treatment optimization and membrane reactor testing. Samples were collected and delivered to Water laboratory on the same day and preserved in a cold room.

Table 11 Laboratory analysis conducted by Water Laboratory, Aalto University

Parameters	Standard Procedure
Suspended solid	SFS-EN 872, dated 2005; Whatman GF/A – glass fiber filter

Total Nitrogen	SFS-EN ISO 11905-1, dated 1998 + Standard Methods (dated 2005) 4500 B. Ultraviolet Screening Method + Ganimede N device instructions
Ammonium nitrogen (NH ₄ -N)	ISO 11732 (flow injection method), dated 2005
Total phosphorus	Oxidation: SFS-EN ISO 6878, dated 2004; Measuring: SFS-EN ISO 15681-1 (flow injection method), dated 2005
Orthophosphate (PO ₄ -P)	Measuring: SFS-EN ISO 15681-1 (flow injection method), dated 2005
Total solid (dry matter + organic matter)	SFS 3008, dated 1990 (only in Finnish)
Turbidity	SFS-EN ISO 7027, dated 2000
pH	SFS-EN ISO 10523, dated 2012
<i>E.coli</i>	SFS-3016, dated 2011

The metals were analysed for dry sludge was done by using SFS-EN-ISO standard procedure in chemistry department of Aalto University.

4.6 NPHarvest process flow design for continuous flow

The first objective of this work was to design the process flow of NPHarvest technique for continuous treatment. NPHarvest technique is a combination of pre-treatment and nutrient recovery process. The process designing was based on 1B and 1D report done by Juho Kaljunen and Simon Reuillard research members of NPHarvest team. This work was to combine 1B and 1D work and design pre-treatment process from batch test to continuous flow. A schematic flow diagram of the pre-treatment unit is followed by a nutrient recovery unit. In the nutrient recovery process, pH adjustment for continuous flow was added in the process. A Process flow diagram of NPHarvest technique is shown in Figure 7 which treats liquid waste for continuous flow.

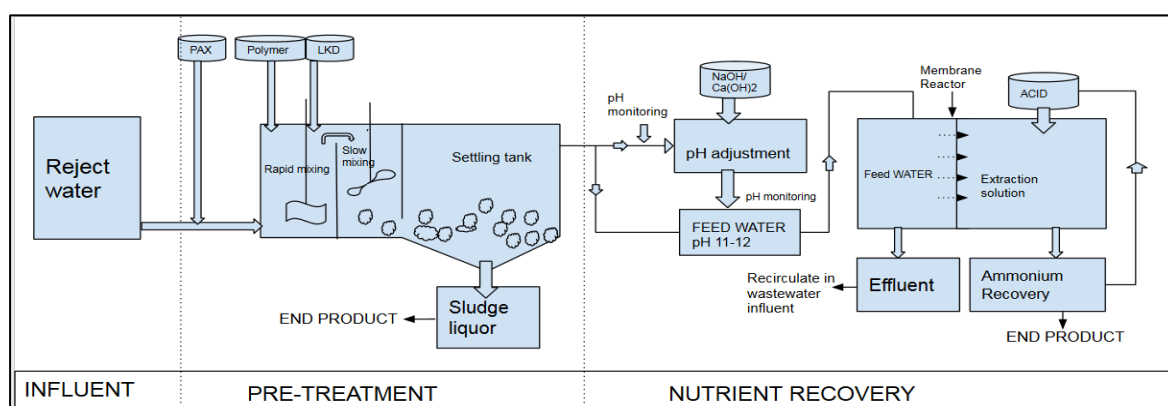


Figure 7 Process flow design of NPHarvest technique for continuous flow

Pre-treatment process has three steps, i.e. coagulation, flocculation and ballasted sedimentation. In Figure 7 reject water (influent-1) storage tank was connected with a pipe to rapid mixing unit and the first chemical coagulant dosed in the pipe. The arrow in the process flow shows the direction of flow. Rapid and slow mixing use the mechanical mixture. The second chemical flocculent and ballasting agent dosed in rapid mixing tank. The whole pre-

treatment reactor has a close surface at the top and rapid mixing and slow mixing tank are separated by a wall. The flow from rapid mixing to slow mixing is directed from the overflow of the separating wall. The slow mixing tank has a bottom opening to a settling tank. Floc formation occurs in a slow mixing tank and flow is directed to a settling tank. There are two outlets in the settling tank. The bottom outlet collects sediments called as sludge liquor (SL) and the top outlet collects pre-treated water called as pre-treated effluent (effluent-1). The size of rapid mixing, slow mixing and settling tank will depend on the influent flow and retention time and it will be considered during construction. In pH adjustment chamber, NaOH/ Ca(OH)₂ will be used to increase the pH of effluent-1. The pH adjustment has been designed by directing 80 % effluent 1 flow to increase pH in adjustment tank and 20% flow connected to feed-water to regulate the pH of feed-water in between 11 - 12. The pH adjusted tank has been connected to the feed-water chamber and pH adjusted water is called feed-water (influent-2). Currently, pretreated effluent-1 flow to feed-water will be regulated by the mechanical valve. In the future, it will be replaced with a sensor valve to regulate flow according to pH monitor sensor in the feed-water chamber. Influent 2 has been connected to the membrane reactor. The membrane reactor has two compartments separated by a hydrophobic membrane. One chamber has been connected with feed water and another chamber has been connected with an acid solution which is also called an extraction solution (ES). Detailed information of membrane reactor structure is in the 1b report (Kallonen *et al.*, 2018). After increasing pH of feed-water ammonium in feed-water is converted to ammonia and it volatilizes through the membrane interface. An arrow line represents ammonia in gaseous form diffusing through the hydrophobic membrane. Ammonia reacts with acid to form an ammonium salt. Extraction solution will recirculate using the pump. Extraction solution will be changed when ammonium salt is saturated. This can be monitored by using an online pH measurement meter. Feed water coming out from membrane reactor is named effluent-2. It will be circulated into influent of WWTP for further removal of nitrogen and phosphorus. Further, Figure 6 design has been used to construct a pilot plant.

4.7 Pre-treatment unit construction

The second objective was to construct a pre-treatment pilot based on NPHarvest process flow design. The pre-treatment unit's shape was re-designed and shown in Figure 8. The pre-treatment unit was constructed in the water laboratory, Aalto University. The re-design of rapid mixing was modified as without mechanical mixer. Figure 8 presents the first modified version of the pre-treatment pilot of NPHarvest technique for continuous flow.

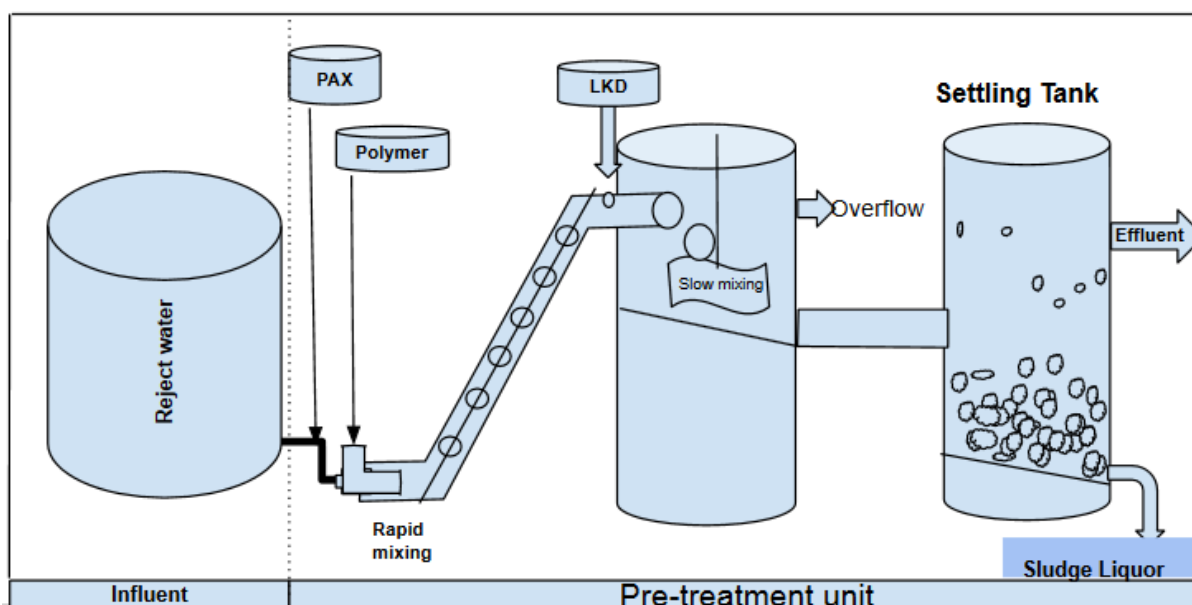


Figure 8 Pre-treatment with rapid mixing modification and bridge between slow mixing and settling tank

The required volume of each unit was estimated on the basis of retention time and influent flow. The retention time was set for rapid mixing 15 seconds, slow mixing 3.01 minute and settling tank 6.02 min (retention time was based on batch test). The influent flow rate was set 100 l/hr. In Figure 8 rapid mixing for coagulant and flocculent was designed without the mechanical mixture to save energy. The rapid mixing tube was made from Acrylics transparent pipe. The pipe length was estimated 35.83 cm (APPENDIX 1), the internal diameter was 30 mm and external diameter 40 mm. Six circular polycarbonates (PC) discs (30 mm diameter and 6 mm thickness, each) was placed in a metal rod and placed inside the acrylic pipe to create turbulence for rapid mixing. Overflow in slow mixing tank was made to stop overflow in settling tank. The bottom part of slow mixing and settling tank has the false base with 45 ° of the inclination for easy transfer of flocs. The material of slow mixing tank was made up of polyvinyl chloride (PVC). The connector between slow mixing and settling tank was fitted with half part PVC and half part acrylic pipe with a screw fitting. Settling tank was made by the transparent acrylic cylinder of 10-liter volume from base to the outflow. The constructed pre-treatment unit has shown in Figure 9.

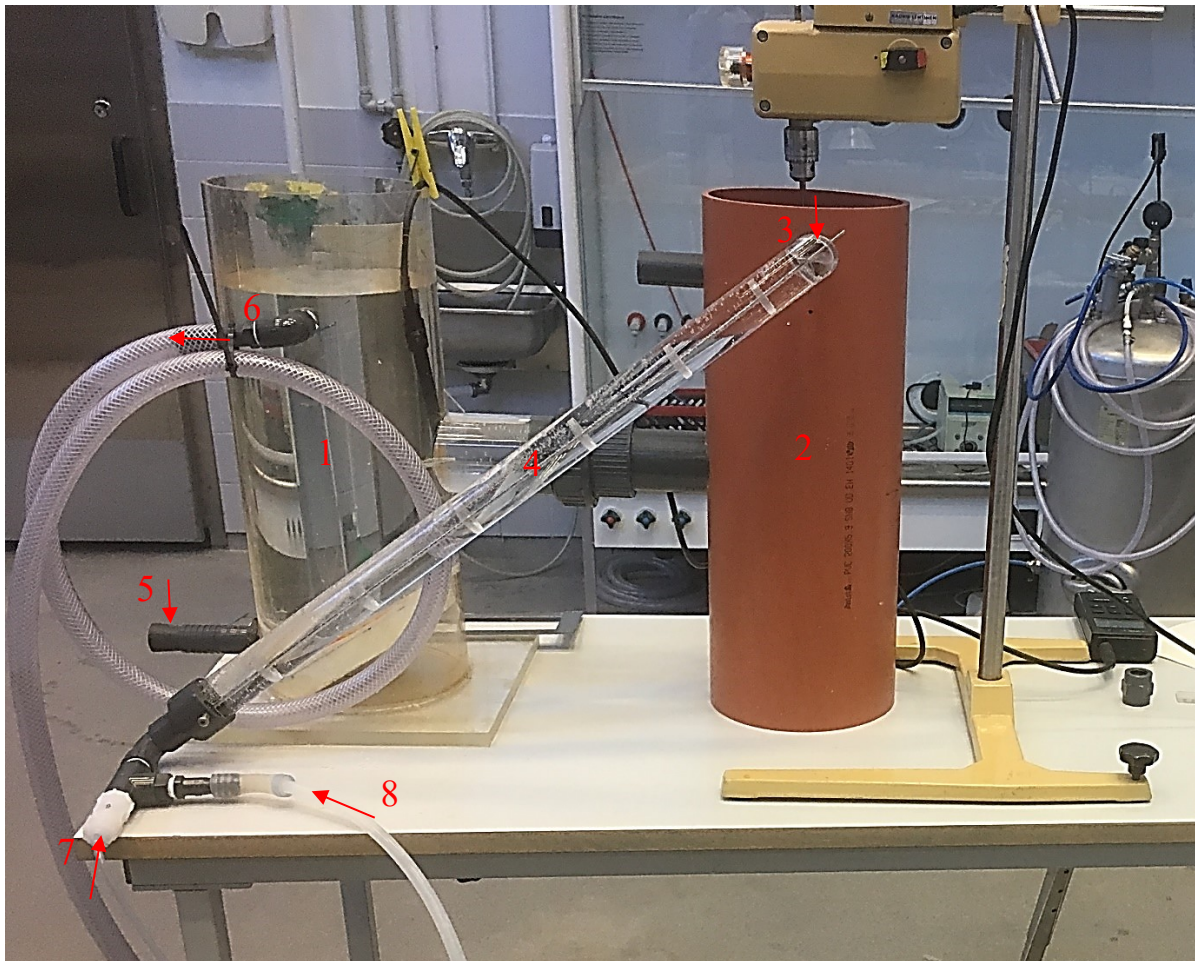


Figure 9 Constructed pre-treatment reactor. Components: 1: Settling tank; 2: Slow mixing tank; 3: LKD dosing point; 4: Rapid mixing tube; 5: Sludge liquor outlet; 6: Effluent-1 outlet; 7: Polymer dosing point; and 8: Influent-1 + Coagulant inlet

During testing pre-treatment, the effluent quality was not matching with expected result. A second rapid mixing was needed and installed. It has also made from Acrylics pipe with 85 ml capacity for 3 sec retention time. Final modified design of pre-treatment has shown below in Figure 14.

The constructed pre-treatment unit works according to our batch test but LKD dosing was not consistent and we needed to work for following issue:

1. Clogging of LKD solution in the pipe.
2. The dosing concentration was not stable.
3. The volume of container was not enough for overnight run.

4.8 Limekiln dust (LKD) dosing unit construction

All the three designs shown in Figure 10 were constructed in the water laboratory, Aalto University. The uniform distribution of LKD in water solution depends on blade type and mixture speed, the outlet and sampling point.

Design 1 A

1. A bucket (capacity not set).
2. Outlet at the bottom of the bucket.

3. Peristaltic pump and tubing of Master Flex L/S 14 (1.6 mm diameter).

Construction material and dimension

A PVC bucket of 8 L capacity was constructed with 90° bend outlet at the bottom of the bucket.

Observation from design 1a

Due to 90° -bend, LKD particle deposited in the outlet fitting. Dosing was also small that there was not enough velocity to carry the entire LKD particle, which cause blocking in the tube. Outlet was closer to the bottom where LKD deposition also blocks the outlet.

Design 1B

The outlet was sifted 10 cm above and straight outlet fitting from the design 1a.

Observation from design 1b

Still LKD clogging in the tube. Outlet fitting and pump tube connected using thicker pipe, where the gap between outlet fitting and pump tube also cause deposition of LKD and result in clogging. Design 1a/b capacity was also not suitable for long run pilot operation.

Design 2 (constructed on the following basis)

1. Design for enough solution capacity for an overnight run.
2. The propeller should be as low as few mm above the bottom of the container
3. The pump tube connection should be of bigger diameter than the outlet fitting.
4. Pump tubing selected Master flex L/S 15 (4.8 mm diameter)
5. The shortest distance in between LKD container and LKD dosing point.
6. LKD container and pumping on the same height.
7. After the pump, LKD flow should be under gravity flow.

Construction Material and dimension

Design 2 was made form acrylic transparent cylinder. Total height of container was 100 cm, inner diameter 20 cm and have the full capacity of 31.4 liters. We can only run with 27 L solution because of mixture speed. The outlet was at the bottom of the LKD container.

Observation from design 2

No clogging in the tube but LKD dosing concentration was increasing with time.

Design 3 (following modifications in design 2)

1. Two mixing blades at 10 cm distance difference in same rod was placed for proper mixing.
2. Outlet was placed 20 cm above the bottom. Sampling point was placed in between wall and mixture shaft.
3. Lower part of the container 6.2 L was a dead zone, LKD solution cannot be pumped from this area.
4. LKD container was placed higher than the pump and pilot to avoid clogging in the tube

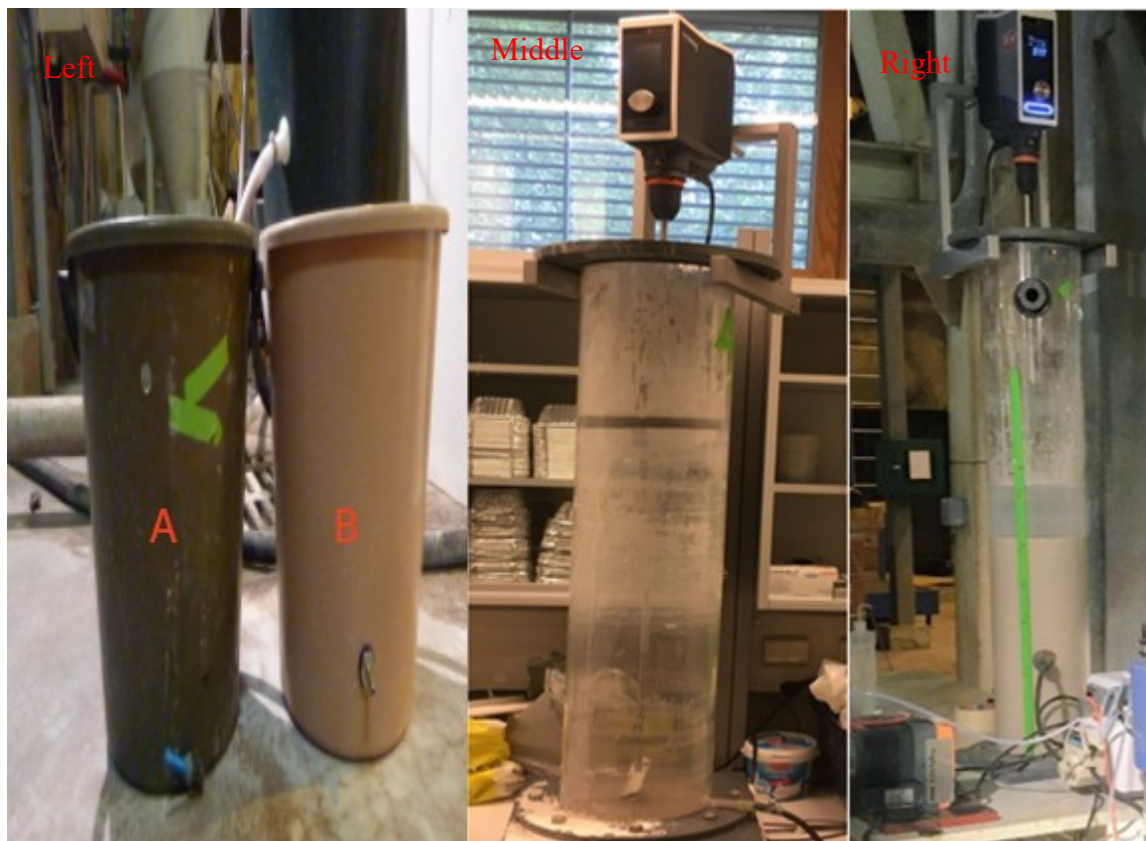


Figure 10 Left: Design 1 (A and B): First LKD dosing container. Middle: Design 2: modification in container and blade. Right: Design 3: Modification in outlet

Observation:

LKD dosing works well with following mixture rotation setting:

- >20 L LKD solution: Mixture rotation 315 rpm
- <20 L LKD solution: Mixture rotation 215 rpm

4.9 Pre-treatment operation

The reject water from Viikinmäki was used as sample to study pre-treatment pilot performance.

Experimental unit

A constructed pre-treatment pilot was used for solid removal of reject water. Figure 11 shows pre-treatment unit setup at Viikinmäki WWTP.

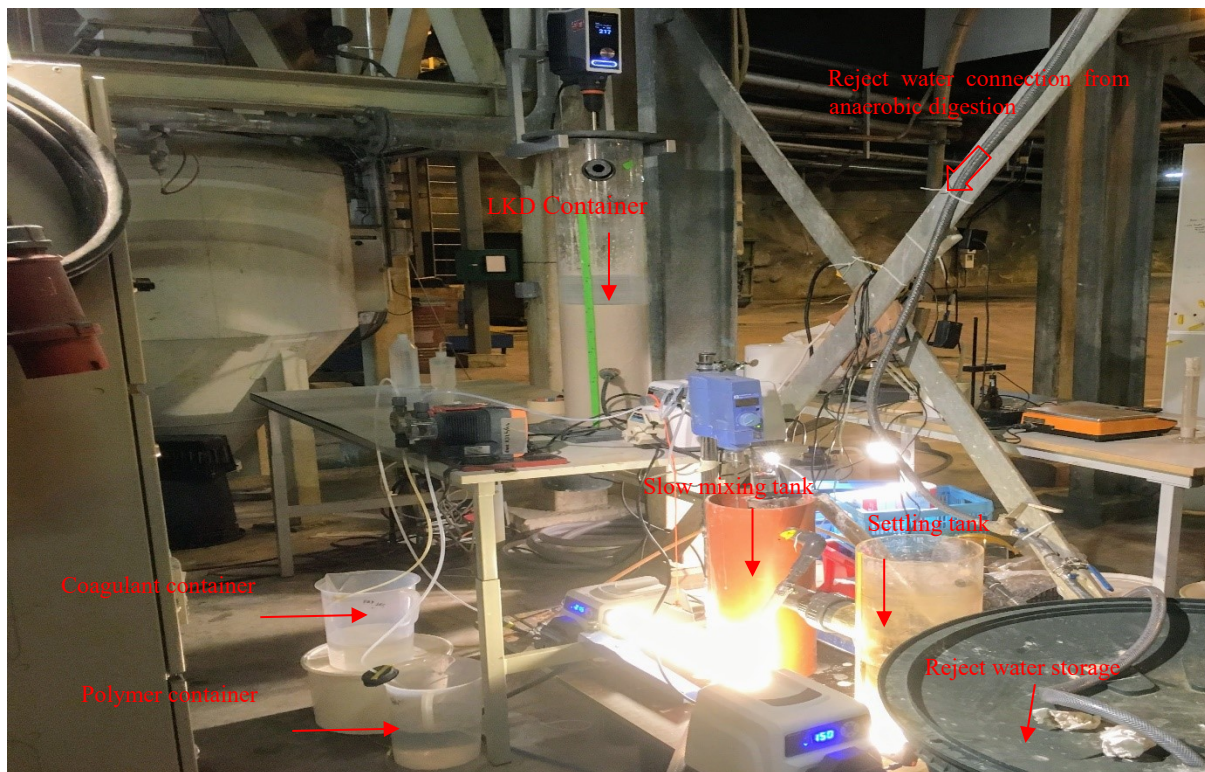


Figure 11 Full set-up of Pre-treatment

A reserve tank of 100 L storing capacity container was receiving reject water from settling tank of bio-digester. The reject water flow to storing tank was under gravity flow and control valve used to control the flow. One peristaltic pump was applied to pump reject water from storing container to the rapid mixing unit. The three different chemicals were used, i.e. Coagulant (PAX XL 100), Polymer (SUPERFLOC A120) and Limekiln Dust (LKD) for ballasted sedimentation. The first coagulant was dosed in the influent-1 pipe after the peristaltic pump. The coagulant reduces the repulsion between colloidal particles. The second chemical, polymer dosed at the beginning of rapid mixing tube. The third chemical, LKD pumped at the end of the first rapid mixing tube followed with second rapid mixing unit. The second rapid mixing unit followed to slow mixing tank. The floc grows bigger in slow mixing and LKD particle combined with flocs to help in ballasted sedimentation. The slow mixing tank was followed with a settling tank. The sludge liquor collected from the bottom outlet and effluent-1 from the top outlet. The effluent -1 further used for nitrogen recovery.

Initial setting for each set of experiment:

Each set of experiment was started with an initial setting. The influent flow and chemical dose are the variables of the experiment. All set of experiment was followed same steps before sampling.

1. Adjustment of required chemical dosing by the pumps.
2. Start to pump required influent flow.
3. Set effluent-1/ sludge liquor (SL) outflow ratio was set to 65/35%. (SL outflow was controlled with a pump so only SL outflow needs to be adjusted)
4. After adjusting SL pump flow, let the pump running.
5. Wait until effluent-1 outflow starts.
6. Sampled at time 0 made (before chemical dosing start) and

7. Then start all three chemical dosing pumps at the same time. Sampling points are shown in chapter 4.4.

Experimental procedure:

The experiments were performed in three steps. In the first step, finding the optimal chemical dose to achieve < 200 mg SS/l in effluent-1. The chemical dosing ranges: PAX XL 100 (0.7 – 2.8 g/l), Super floc A120 (0.7 – 2.8 mg/l) and LKD (2 – 6.5 g/l). During chemical optimization, 90 l/h. flow rate was used. This high and low chemical dose shown in Table 12 was taken from 1D report. The chemical dose in pre-treatment pilot might change to achieve the required effluent quality (< 200 mg SS/l).

The second step of the experiment was to cross-check the optimal dose with an influent flow rate of 60, 90 and 120 l/h.

The third set of experiment was to determine total solid content in sludge liquor with optimal chemical dosing based on influent flow rate.

4.10 Nutrient recovery operation:

Liqui-Cel 3M membrane contactor was purchased for nitrogen recovery. The experiment was performed in batch test to study contactor performance.

Sample preparation

The pH of effluent-1 water was increased using NaOH from pH 8.1 to >11 and mixed with the help of magnetic stirrer at low speed. The flocs formed after pH increased was left stable for 20 min to settle the flocs. The supernatant with > 11 pH was termed as feed water (influent-2) and used for nitrogen recovery.

Experimental unit

A nutrient recovery setup shown in Figure 12 was arranged according to the schematic diagram of ammonia recovery using Liqui-Cel 3M membrane contactor was shown in Figure 14. Pre-treatment effluent-1 water was brought to Aalto water laboratory to use as influent-2 for membrane contactor. One peristaltic pump with two pump head fitting was used to pump influent-2 water through the lumen side of hollow fiber membrane and extraction solution containing sulfuric acid pumped counter current through the hollow fiber membrane. A bucket with eight-liter capacity was used for influent-2 storing and covered with a lid to prevent from ammonia escaping. A water bath was used to maintain the temperature at $34\text{ }^{\circ}\text{C}$. Extraction solution was placed in a closed glass bottle of 500 ml

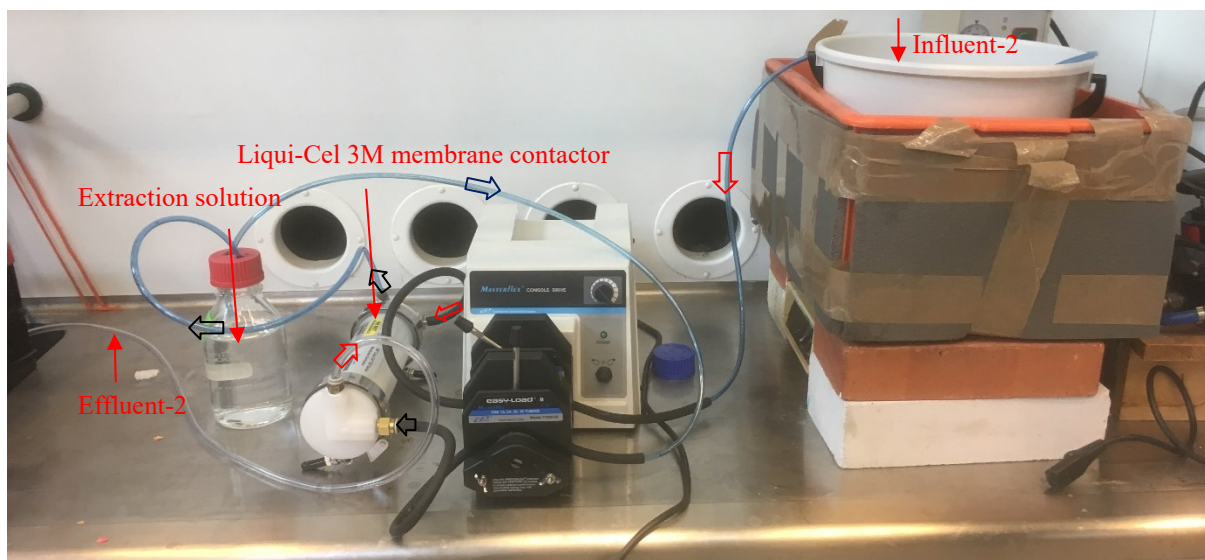


Figure 12 Setup for nutrient recovery using Liqui-Cel 3M membrane contactor

Liqui-Cel 3m Membrane Contactor

This device contains microporous hollow fiber membrane inside a device designed. It has large surface area for stripping dissolved gases. This extra flow (EXF) series, feed water flows around the outside of the hollow fiber membrane. 'The gas difference concentration outside the shield of hollow fiber membrane and inside lumen drives rapid and efficient dissolved gas transfer. A baffle in the middle of the reactor direct liquid radially across the membrane array' (3M Liqui-Cel, n.d.). Figure 12 shows the internal structure of the membrane contactor.

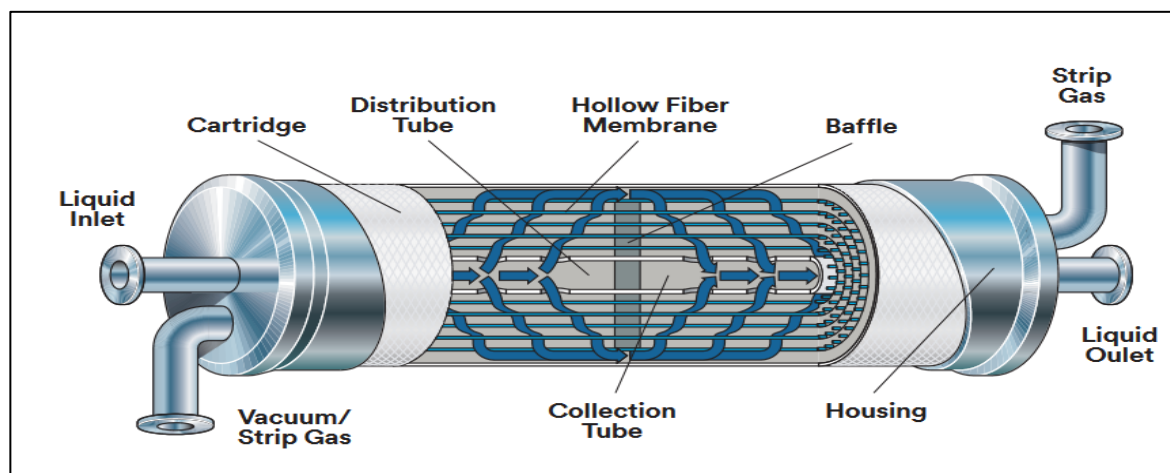


Figure 13 Internal design of 3M Liqui-Cel membrane contactor.

In this experiment, I used sulfuric acid to circulate through the hollow fiber membrane. The principle is the diffused ammonia from tube to hollow fiber membrane and reacts with sulfuric acid to form ammonium sulfate. Recovered ammonium as ammonium sulfate can be used as raw material for nitrogen fertilizer and some other industrial purpose.

Specification of membrane contactor

Brand	Liqui-Cel™
Diameter	64 mm

Industries
Length
Series

Bioprocessing
203 mm
Liqui-Cel EXF series

Initial setting for each set of experiment:

1. The effluent water was gently stirred using magnetic stirrer and 4 Molar NaOH solution was used to rise the pH (>11).
2. The magnetic stirrer was stopped and let the flocs to settle for 20 min.
3. The flocs were separated from water by decantation.
4. The decanted water was continuously pumped through membrane contactor.
5. 0.6 Molar H_2SO_4 solution was used as the extractor solution. The extractor solution was re-circulated during the experiment.
6. The influent-2 and extraction solutions was pumped 100 ml/min and sampling was done zero-minute sample with every 10-minute interval.
7. The influent-2 passing through membrane contactor and coming out as effluent -2 collected in another bucket.

Experimental Procedure:

The experiment was performed and analyzed sample. The sample was taken during experiment to estimate ammonia removal and recovery rate.

5. Results

5.1 NPHarvest pilot and functional pre-treatment unit

After several sketch drawn for NPHarvest technique process design, the final 2D design is presented in Figure 14. This NPHarvest technique process design is the outcome of batch process to continuous process

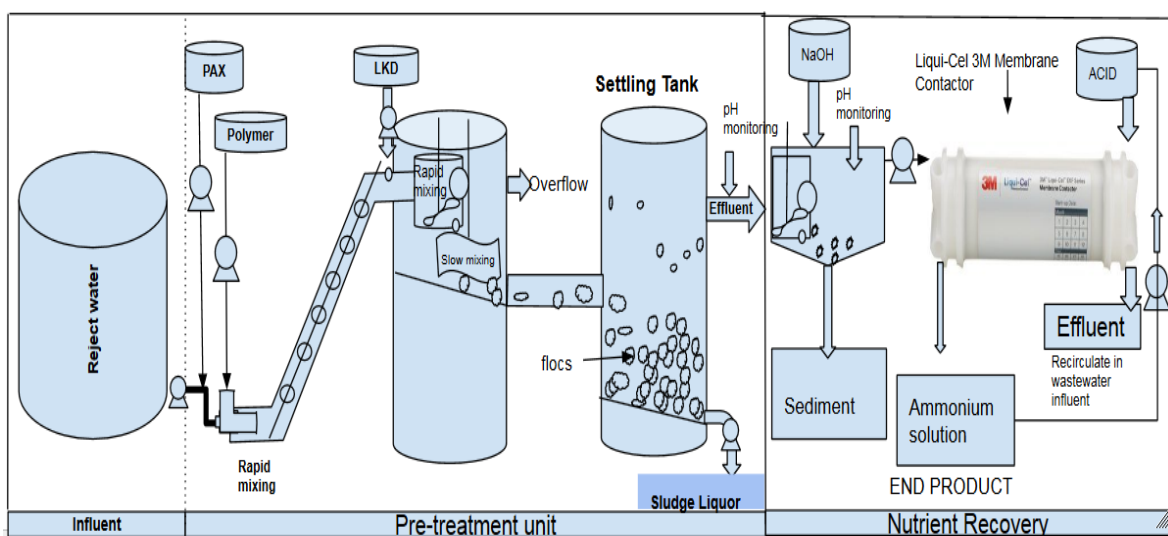


Figure 14 NPHarvest technique process design for continuous flow

This thesis presents a successful construction of pilot scale pre-treatment unit of NPHarvest technique for continuous flow. The pilot designed capacity was to treat 100 l/hr. influent water.

The constructed pilot scale pre-treatment unit was fully functioning. The challenges learned during construction and testing the pilot plant will help while scale-up to full-scale treatment plant.

5.2 Pre-treatment process

5.2.1 Chemical dose optimization and process stabilization

Several chemical combinations were tested but some best combination of chemicals dose are presented in Table 12. The test was performed with 90 l/hr. influent flow rate.

Table 12 Various chemical dose combination

Chemical dose combination	PAX (g/l)	Polymer(mg/l)	LKD(g/l)
Low (recommended in 1D report)	2	2	2.5
High (recommended in 1D report)	2.5	2	3
A	2	2	3
B	1.6	2	4
C	1.6	1.6	4
D	1.3	1.3	3.5
E	0.7	0.7	2
F	2.6	2.6	6.5

Figure 15 presents the influent and effluent SS concentration with various combination of chemical dose. The result shows that chemical dose combination D (Table 12) gives effluent SS concentration below 200 mg/l. The influent SS concentration in the graph is the mean concentration during chemical optimization. The continuous process uses 30% less coagulant and polymer than the recommended chemical dosing from 1D report to achieve the targeted effluent-1 SS concentration (<200 mg SS/l).

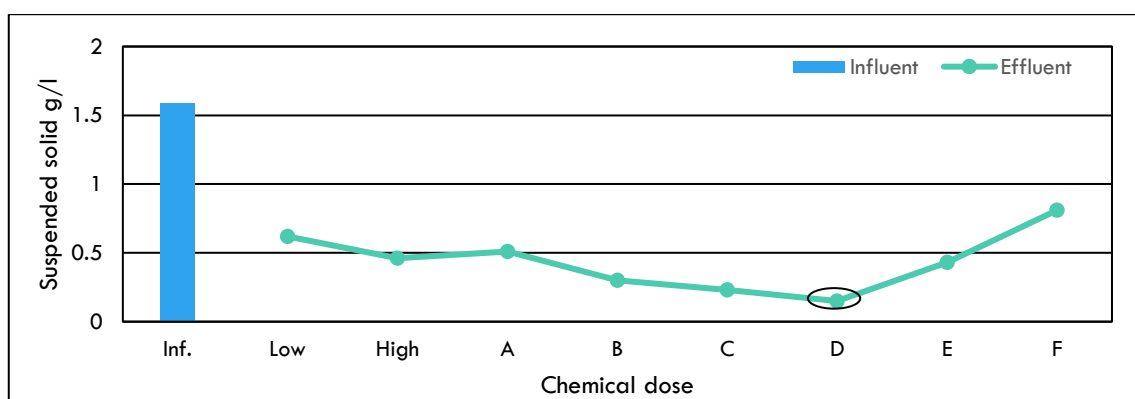


Figure 15 Various combination of chemical dose for suspended solid reduction in pre-treatment

Figure 16, experiment was performed based on optimized chemical dose D (Table 12). The experiment was started with preset explained in chapter 4.5.

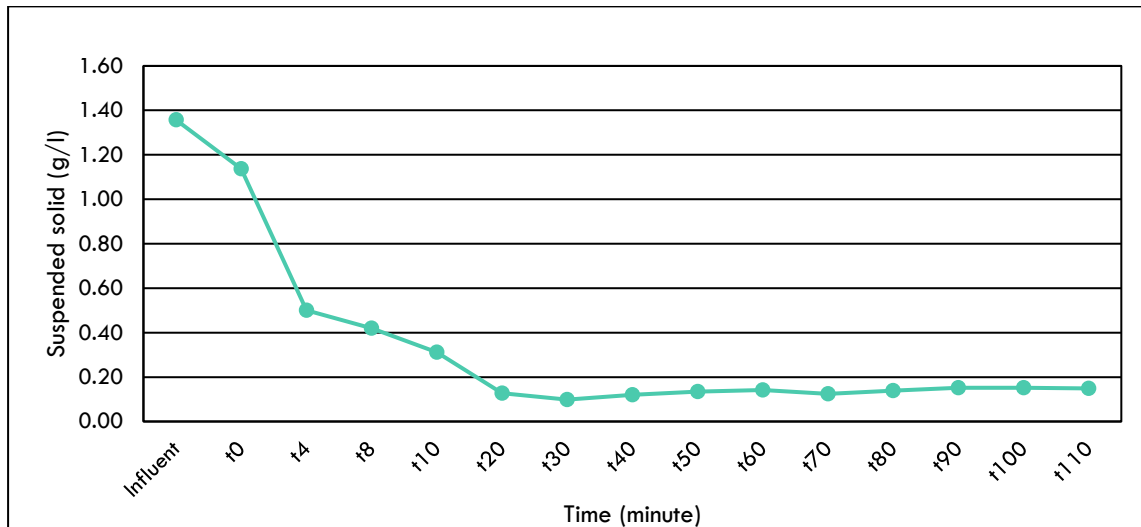


Figure 16 Stabilization of effluent-1 (SS concentration) during pre-treatment

The stabilization of the process was achieved at 20 min which was twice of retention time (sum of slow mixing and settling tank retention time). The stabilization result was informative for the proper time to use effluent -1 for nutrient recovery. Pre-treatment was followed with nutrient recovery where SS concentration is important. Effluent-1 quality was accepted for nutrient recovery after the process stability. The effluent-1 sample at time zero shows less SS concentration than influent. Due to pumping rate it takes certain time to fill the pre-treatment unit with influent. The difference of SS in influent-1 and zero sample shows that some of settleable particles settle if it let stable.

5.2.3 Pre-treatment pilot performance in different flow rate

The test was performed with three influent rate 60, 90 and 120 l/hr. The Figure 17 shows the effluent quality with optimal chemical dosing with respect to influent flow.

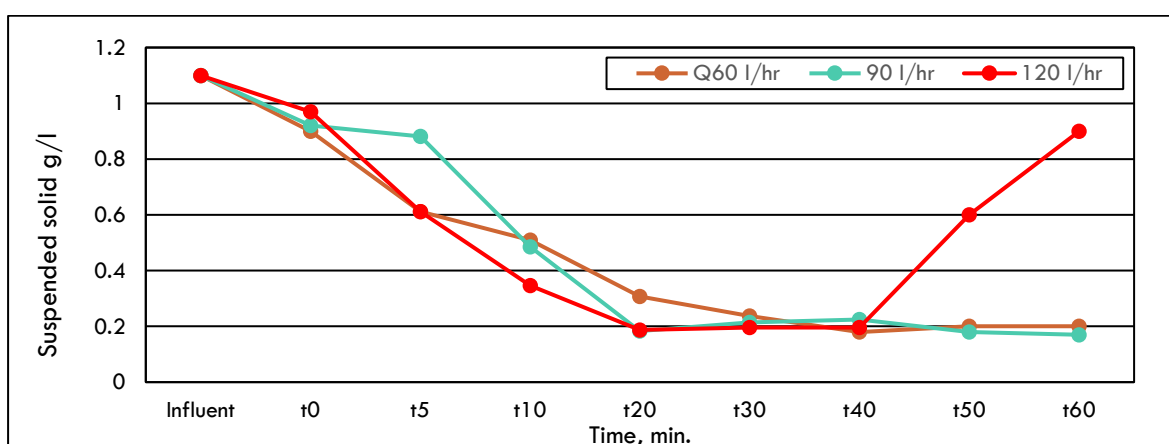


Figure 17 Effluent quality with optimal chemical dose with respect to influent flow rate.

Changing the flow rate will change the retention time. The obtained result presents that pilot performs very well with Q90 and effluent -1 SS concentration stays stable 20- 60 minutes. The

test with Q60 took 30 minutes to get stable effluent-1 quality. The SS reduction with Q 120 l/hr. was followed a similar pattern of SS reduction with Q60 and Q90 until 40 minutes after that effluent -1 SS concentration starts increasing. The retention time set for rapid mixing and slow mixing also works well even time decreases by 30%. However, the optimal flow rate for optimum chemical dose was found at Q90.

5.2.4 Total solid in sludge liquor at optimal chemical dose

The sludge liquor removal rate was set 35% of influent flow and Figure 18 presents the sludge liquor total solid concentration. The total solid (TS) is the sum of fixed solid and volatile solid. Fixed solid (FS) is inorganic matter and volatile solid (VS) is organic matter. The graph in the Figure 18 shows no clear difference in TS concentration variation with different flow rate.

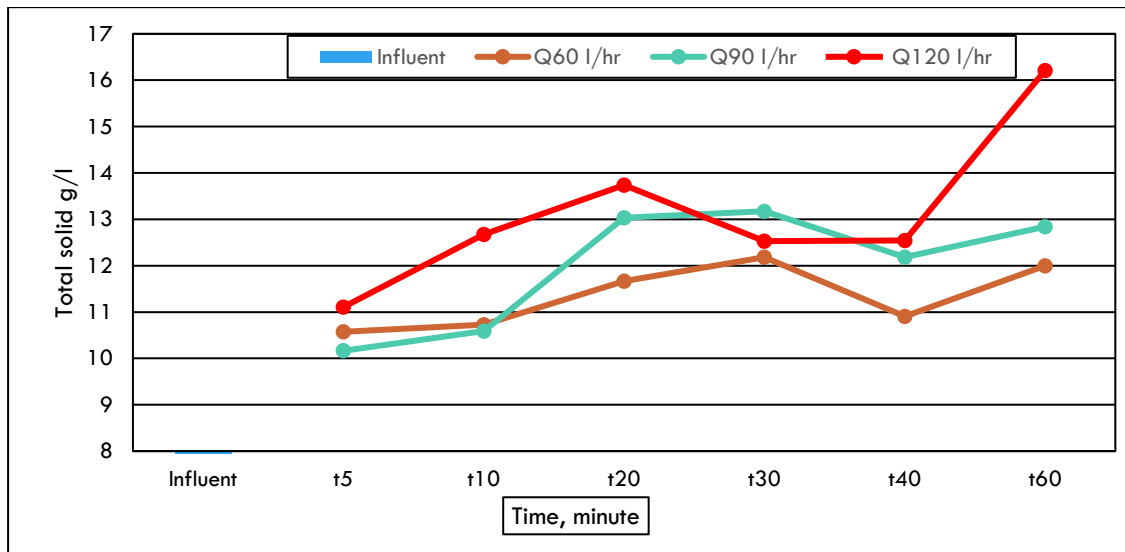


Figure 18 Sludge liquor total solid concentration

The averages sum of total solid in SL is presented in Figure 19. In all three different flow rates, the VS concentration in SL is almost same. Fixed solid increases with increase of influent flow rate. This is because LKD dosing increases with flow rate, which results the increase of FS with increasing of influent flow rate. A short period of the experiment (< than 60 minutes.) does not give any distinction with settling rate disturbance due to in influent flow rate.

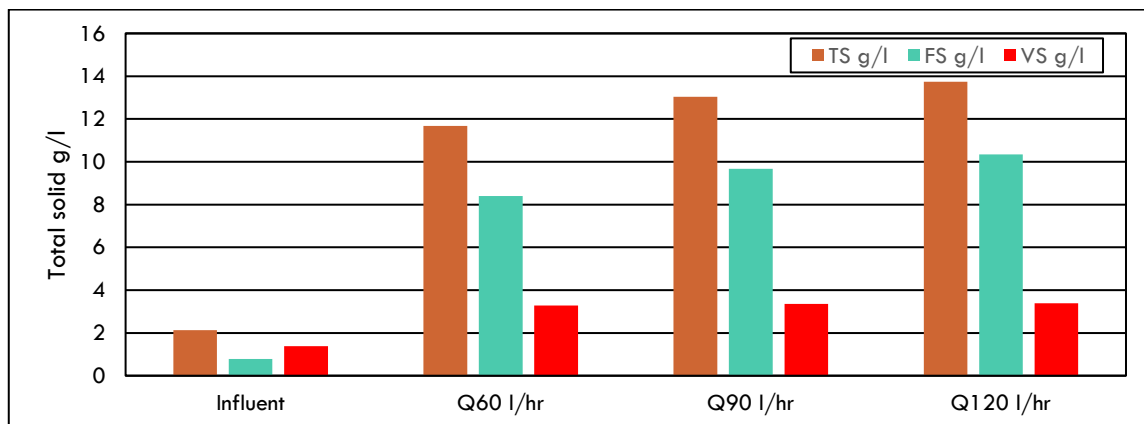


Figure 19 Average sum of Total solid (FS + VS) in sludge liquor 20-60 minute.

5.3 Comparing efficiency of limekiln dust_{ty} and limekiln dust_r

Visually LKD_{ty} contains more fine particles than in LKD_r. LKD_{ty} and LKD_r were from different place so, their efficiency in our process was compared based on SS concentration in effluent-1 and TS concentration in SL. In Figure 20a both LKD produce SS concentration < 200 mg/L in effluent -1. In Figure 20b TS concentration was higher using LKD_{ty} then LKD_r. The difference in TS concentration was of 3.7 g/l.

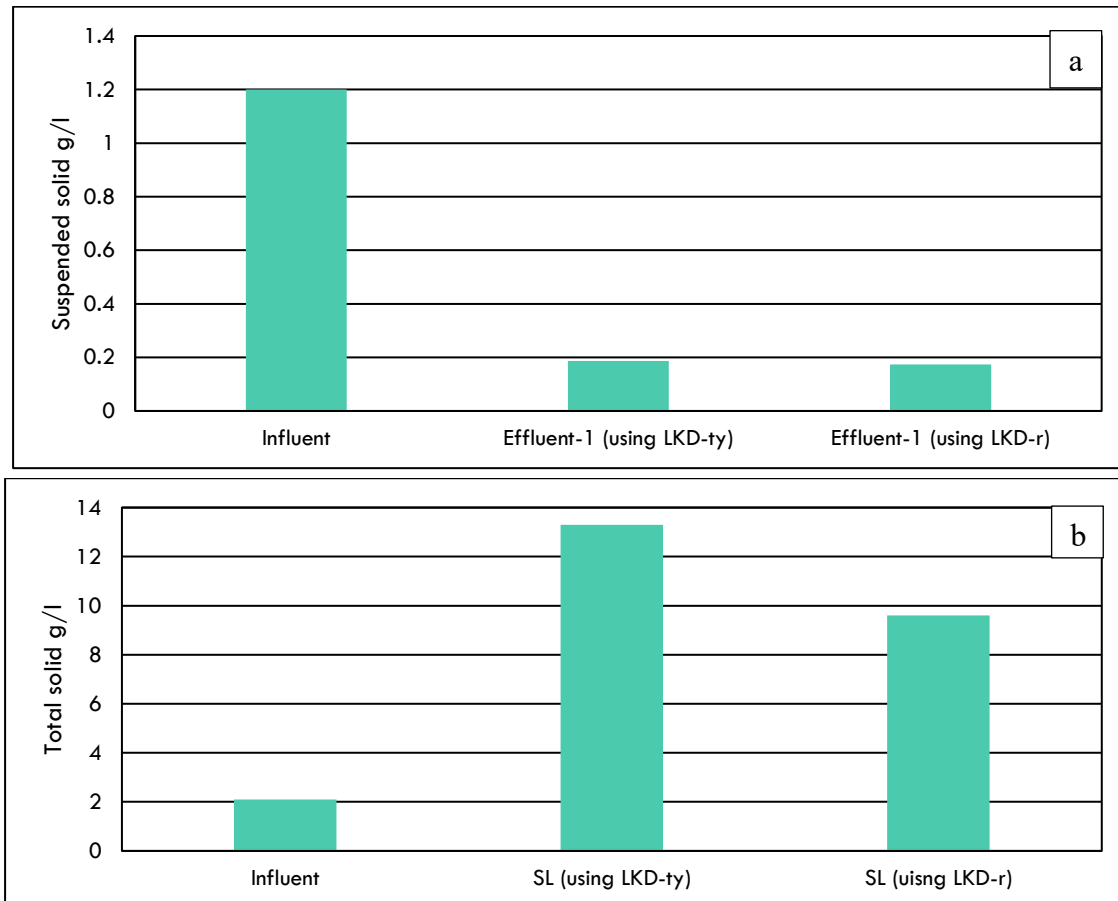


Figure 20 (a) comparing SS concentration in effluent. (b) Comparing TS concentration by using LKD_{ty} and LKD_r

Sludge liquor bed (SLB) was the sludge volume in settling tank. The SLB height was measured during the experiment to analyses the settling rate of flocs. Figure 21 presents the sludge liquor bed growth with time.

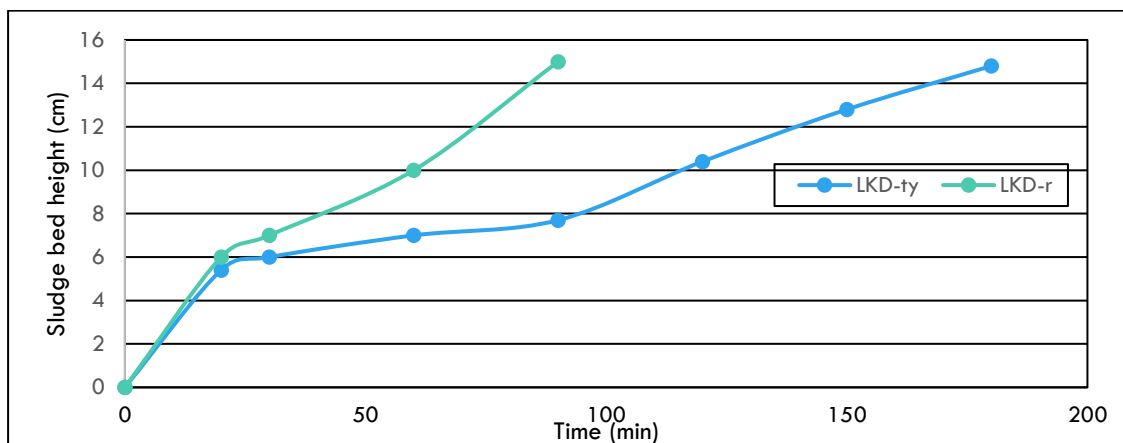


Figure 21 Comparing sludge liquor bed (SLB) height using LKD-r and LKD-ty

Both LKD types showed similar sludge liquor bed height until the time of stabilization. The maximum SLB was set 15 cm to control effluent quality. By the use of LKD_r SLB rises to 15 cm in 1-hour experiment but LKD_{ty} took two and half hour to reach 15cm SBL. LKD_{ty} shows flocs settling quicker than LKD_r. Even both LKD gives similar effluent quality but due to sludge settling LKD_{ty} is a better option for our pilot. The difference in flocs settling might also depend on the influent quality.

5.4 Ammonia recovery using Liqui-Cel 3M membrane contactor

The ammonia was recovered in the extraction solution. The ammonia recovery rate in the extraction solution was linear up to 30 min and recovery rate increases three times higher in 30 to 40 min. The overall result shows ammonia removal rate was 86% and the recovery rate was 78%. The recovery rate could have increased if performed with a smaller flow rate (<100 ml/min). Figure 22 shows the recovery and removal of ammonia from the feed-water.

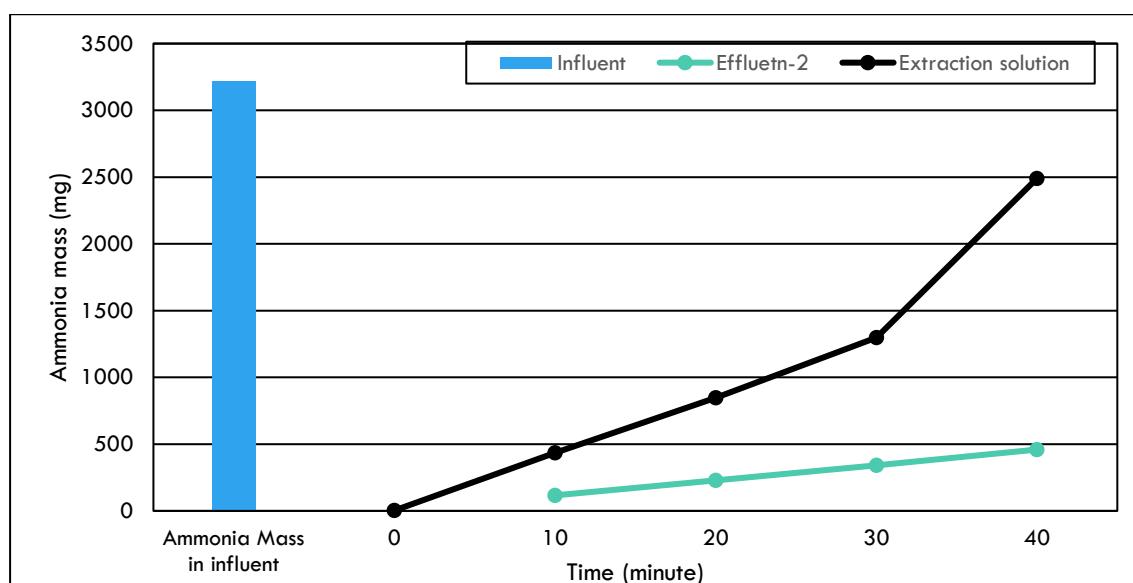


Figure 22 Liqui-Cel 3M membrane performance using feed-water.

SS concentration in influent-1 was 167 mg SS/l, which was reduced to 30 mg SS/l in effluent-2. At the end of the experiment, SS losses were ended in a membrane reactor. The SS stocked

in membrane reactor might block the pore of the membrane and decreased the harvesting efficiency of membrane contactor with time. This membrane contactor is not suitable for NPHarvest project.

5.5 Sludge quality analysis

Sludge Liquor from pre-treatment contains 98.7% water and it should be dewatered (20-30 % TS) for further use. The concentration of harmful metals and pathogen in sludge should meet to use as the fertilizer product act 539/2006. Decree of the ministry of agriculture and forestry of fertilizer products 24/11 has drawn the line on the requirement for each type of fertilizer product. Table 13 present's nutrient and metal concentration before and after pre-treatment and compared the limit value for metals in fertilizer product and also analyses the hygiene quality of SL.

Table 13 Nutrient and metal analysis from dry solid sample and hygiene quality (*E. coli*) in sludge liquor.

	Influent-1 (dry solid)	Sludge liquor (dry solid)	Maximum allowed Concentration Finnish Water Utilities Association publication series no. 69 Finnish Industrial Wastewater Guide –conveying non-domestic wastewater to sewers
Total. N (mg/g)	33	22	
Total. P (mg/g)	3.3	1.8	
Metals (mg/g)			
K	50.6	139	-
Mg	20.6	4.6	-
Ca	61	238	-
Cd	<0.05	<0.05	0.0015
Pb	<0.1	<0.1	0.1
Cu	<0.05	<0.05	0.6
Zn	<0.05	<0.05	1.5
Cr	<0.1	<0.1	0.3
Ni	<0.1	<0.1	0.1
As	<0.05	<0.05	0.025
Hg	<0.1	<0.1	0.001
Hygiene quality			
Bacterial count (<i>E. coli</i>)	Influent (reject water)	Effluent	Sludge liquor
Average (cfu/ml)	2016	1250	1770

The nitrogen and phosphorus in dry sludge have nutrient value. The increase of calcium in dry sludge was due to using of LKD (lime product). Potassium and Magnesium in dry sludge are

also an important nutrient for plant growth. All the metal concentrations were below the detection limit of the used method. The hygiene quality of SL was tested by making *E. coli* plate count. The bacterial count has analyzed from influent, effluent and sludge liquor and the result shows no significant amount of *E.coli* reduction during pre-treatment. Decree on Fertilizer products (24/11) have pathogen limitation (*E.coli*) <1000 cfu/g. This analysis is not valuable when SL still need further treatment. This result might be useful in future to compare with final product of sludge.

5.6 Mass flow of nutrients and solid in NPHarvest treatment

Table 14 presents the loss, recovery, and removal percentage of different variables/nutrients in the whole process and in different units. In the whole process, suspended solid removal was 89% where 82% has removed in pretreatment and 18% of suspended solid passing through Liqui-Cel 3membrane. The 91% of 18% SS remain in the membrane reactor, which could block the membrane pore and decrease the efficiency in ammonia harvesting. TP removal was 85% in which 81% of TP was removed in pre-treatment.

The Liqui-Cel 3membrane shows 78% ammonia recovery efficiency using influent -2 (167 mg SS /l). In NPHarvest process ammonia recovery efficiency was calculated 40% from mass flow calculation. In pre-treatment ammonia loss was zero and in membrane contactor, 8% ammonia was lost during the recovery process.

Table 14 Nutrients and suspended solid mass flows

%	NPHarvest	Pre-treatment	Nutrient Recovery
Removal			
Suspended Solid	89	82	91
T. Phosphorus	85	81	32
NH ₄ -N	48	35	25
Loss			
NH ₄ -N	4	0	8
Recovery			
NH ₄ -N	40	0	78
Mass balance			
	In (mg)	Out (mg)	%Error
Suspended Solid	1500	1351	9.94
NH ₄ -N	810	775	4.33
T. Phosphorus	13	12	8.62

The mass balance calculation gives <10 % error with SS, NH₄-N and TP. The detail calculation of mass flow is presented in APPENDIX 2.

5.7 Operational cost using NPHarvest technique

NPHarvest technique is a continuous treatment process. The operational cost include cost for chemical and electricity. Electricity was consumed by pumps and mechanical mixture and it was used in the process and chemical preparation. The investment cost in constructing pre-treatment unit and nutrient recovery unit was not included. Table 15 and 16 present the NPHarvest technique treatment cost based on chemical and electricity used to treat 1 m³ of Viikinmäki reject water.

Some hypothesis was assumed in calculation.

- 1) Influent flow for treatment process 100 l/hr.
- 2) Optimal chemical dose D was used for the process.

Table 15 Pre-treatment cost estimation (per m³)

Chemical cost estimation to treat per m ³ reject water of Viikinmäki				
Chemical	Amount (g/m ³)	Price (€/tons)	Cost (€/m3)	
PAX XL100	1300	250	0.32	
Super floc A-120	1.3	2500	0.01	
LKD	3500	30	0.10	
Price for chemical consumption			0.43 €	
Energy cost estimation				
Electric appliances	Number	Power (Watt)	Time (hr.)	Electricity consumption (Watt hour, Wh)
Diaphragm pump	2	12	10	240
Peristaltic pump	3	75	10	2250
Mixture (for slow mixing tank and LKD mixing)	2	90	10	1800
Mixture (for small rapid mixing)	1	5	10	50
Electricity consumption during pre-treatment				4340 Wh
Electricity price for household in Finland				0.15 €/KWh
Price for electricity consumption				0.65 €
Total price				1.08 €

Table 16 Nutrient recovery cost estimation (per m³)

Chemical cost	Consumption	Price	Cost (€)
NaOH	4.16 kg	376 €/tons	1.56
H ₂ SO ₄	1.28 L	0.3 €/l	0.38
Price for chemical consumption			1.94 €
Energy cost estimation			

Electric appliances	Number	Power (Watt)	Time (hr.)	Electricity consumed (Watt-hour, Wh)
Peristaltic pump for pumping feed-water and extraction solution	1	75	10	750
Mixture (for pH adjustment)	1	30	10	300
Electricity consumption in Nutrient recovery				1050 Wh
Electricity price for household in Finland				0.15 €/KWh
Price for electricity consumption				0.16 €
Total price				2.10 €

The total cost to treat 1 m³ reject water using NPHarvest technique cost 3.18 € (sum of total price from Table 15 and 16) or 5.10 €/kg NH₄-N recovery (calculated as 78 % recovery efficiency of membrane contactor). In pre-treatment chemical consumption was estimated on the basis of optimal chemical dose. The electricity consumption was calculated based on the power consumption of the appliances. The price for chemicals used in pretreatment was taken from the 1D report, Sulphuric acid price was taken from the 1B report and NaOH price was taken from Alibaba webpage. NaOH consumption was calculated by making an experiment in water laboratory. Sulphuric acid (98% pure) consumption was calculated theoretically to saturate the amount of ammonia in 1 m³ reject water of Viikinmäki. The cost may vary with the ammonia concentration in reject water. The detail estimation of NaOH and H₂SO₄ consumption is shown in APPENDIX 3.

6. Discussion

6.1 Challenges in modifying pre-treatment from batch to continuous flow treatment process

The batch process of the pre-treatment was designed for a continuous process. The first challenge was to design an energy efficient continuous process. The rapid mixing was designed without a mechanical mixer. In Figure 14 the rapid mixing unit has obstacles inside the lumen and the flow was uphill. This design replaces the requirement of the mechanical mixer with the physical mixer using the energy dissipated from the head loss.

The pre-treatment uses the ballasting agent to shorten the sedimentation time. The biggest challenge was to minimize the turbulence in the settling tank. The pilot was designed to have one rapid and one slow mixing followed to the settling unit based on the batch process. The challenge was to achieve SS concentration < 200 mg/l (effluent-1) with our designed pilot structure (Figure 8). Therefore, second rapid mixing was installed right after the first rapid mixing which helped to mix LKD and combine with flocs to make it heavier settle fast. This helps in achieving the required effluent quality (Figure 14).

Other challenge was chemical dosing. Two diaphragm pumps have been used to pump a coagulant and a polymer. The biggest challenge was pumping accuracy and a manual adjusting the required flow rate. LKD solution dosing for the continuous flow was not thought quite well before we realized the propeller speed to remain particles uniformly in the solution and clogging problem inside the pipe. The various possible way was applied and finally, need to construct a specific type of LKD tank which is shown in Figure 10 (design 3).

6.2 What are the differences between batch process and continuous flow for NPHarvest pre-treatment technique?

This section answers the research question 2. In the batch process, whole processes took place in a single reactor. The treatment process only started after complete filling the reactor with the sample. The reactor will be kept stable for certain time after completing the process for settling. Effluent and sludge liquor are two different layers in the settling tank and effluent needs to empty first. The chemical dosing is fixed and any changes in chemical doses can only be employed by performing a jar test. The fluctuation in influent quality made difficult to maintain the effluent quality constant and failing the effluent quality cannot use for further process which is wastes of resources and finances (Butler, 2017).

For designing a continuous process, the steps involved in the process needs to be analyzed carefully. If possible, combining the steps lowers the treatment cost. The settling of flocks in settling tank was a big challenge. The continuous flow creates turbulence, which hinders to produce the same ratio of effluent /SL than in a batch process. This caused to flush more volume of SL then in a batch process.

The batch and continuous process were studied for balancing tank volume needed to treat 100 liters influent. The pilot plant was with an operating volume of 15.5 liters. With this capacity pilot plant can treat reject water with the flow rate of 100 l/hr. (excluded first 20 min treatment volume because pilot need 20 min to stabilize effluent quality). In a batch process, we can treat only 42 l/hr. of reject water in 50-liter tank capacity (20 % bigger volume tank required than the sample volume).

6.3 Analysis of pre-treatment unit process

This section answers the research question 3. The pre-treatment of pilot plant is functional and test result supports the feasible for upscaling to an industrial scale. The chapter 6.2 has compared that continuous process need smaller volume reactor and less time to treat similar volume of liquid waste. The batch process would be failed to maintain the effluent quality with change in influent quality. The unit structure of a pre-treatment can linearly increase on the basis of flow rate. The chemical dosing might differ depending on the properties of water. The solid removal in a pre-treatment depends on organic matter concentration and the temperature of liquid waste. The chemical optimization for the continuous process results in 30 % less coagulant (PAX-XL100) and polymer (Superfloc-A120) were used compared to 1D report. The reduction in chemical dosing also support for the conversion from batch to continuous process. One of the reasons can be, 1D report was using the old sample of 21 °C temperature

but, the pilot used reject water of 33 – 34 °C temperature. During the last decade, the most common and extensively used coagulant is with aluminium salt especially poly aluminium chloride (Sahu & Chaudhary, 2013). Poly aluminium chloride has proven more efficient at low dose, wider pH range, the temperature, and colloidal concentration ranges and first choice in the cost and operation (Sinha *et al.*, 2004; Crittenden *et al.*, 2005).

The dosing of LKD was not thought to be serious issue for continuous flow. Chapter 4.8 explain how LKD dosing container was constructed. It took several weeks to understand the need of proper mixing propeller, sampling point and gravity flow of LKD solution to avoid clogging. In NPHarvest pre-treatment LKD was used as a ballasting agent and commercially known as ‘structure lime’ (Nordkalk). The ballasted flocculation increases the floc density and diameter which fasten the flocs settling rate (Lapointe & Barbeau, 2015). Usually, micro-sand as a ballasting agent incorporates into the flocs to make it denser and heavier for quick sedimentation (Tchobanoglous *et al.*, 2003; Young and Eswards, 2003). Ghanem *et al.*, (2007) has reported that the flocs density linearly related to the ballast dose. Microsand is recovered from the sludge by using hydro-cyclone and can be reused for ballasted flocculation process (Ghanem *et al.*, 2007). LKD has a good role in soil improvement, e.g. rise in pH level, rich in calcite or magnesium, absorbent for other nutrients, cuts down the phosphorus runoff from fields (Nordkalk). The dry sludge contains 60% of LKD. The use of LKD in NPHarvest technique gives value to the sludge as fertilizer product.

The Effluent-1/Sludge liquor ratio was to optimize in the process. The stable sludge liquor bed (SLB) height was another issue to optimize. The jar test showed effluent-1/sludge liquor outflow ratio was 80/20 % in 8 min (graph present in APPENDIX 4). The same set of E/SL outflow was not enough to balance sludge liquor and effluent separation in the settling tank. The continuous treatment process makes some turbulence, which decreases the settling time of flocs. The effluent-1/sludge liquor has set to 65/35 % to achieve thicker sludge. The test was also performed with outflow 40/60 % and still observed SLB height growing with time. In the future, the settling tank needs to re-design to reduce the turbulence in settling tank which helps in the better settling of flocs and thicker sludge liquor.

6.4 Evaluation of the NPHarvest technique

This section covers the research question 4 where nutrient recovery technique evaluate on the basis of efficiency of the treatment process. The pre-treatment technique took 10 minutes to treat 100 liters of Viikinmäki reject water. The process produces 65 % effluent and 35% sludge liquor. The optimal chemical dose combination of poly aluminum chloride, super floc, and lime kiln dust gives total phosphorus and orthophosphate removal was 82 and 99.7 % from reject water, respectively. The settling tank had a retention time of 6 min where suspended solid removal was 82 %. Sinha *et al.*, (2002) found that ballast flocculation took two minutes times where conventional coagulation took 30 minutes to settle the particulate matter. Aguilar *et al.*, (2002) studied the coagulation-flocculation process in the slaughterhouse effluent and found total phosphorus and orthophosphate removal using poly aluminum chloride were 99.7 and 100 % respectively. Simoni & Vnucce, (2000) studied coagulation-flocculation using poly aluminum chloride (840 mg/l) in combination with Organopol WPB20 to treat pulp and paper

mill wastewater which gives 91.9 % removal of suspended solids. In NPHarvest technique sludge liquor produced during pre-treatment still contains 99% water which further needs dewatering process to achieve higher solid content sludge. The water removed from sludge liquor can be directed to the nutrient recovery step, which will increase the ammonia nitrogen removal and recovery rate. Zero ammonia nitrogen removal during pretreatment proved from mass balance calculation. The conversion of ammonium to ammonia nitrogen is very small (<10%) since the coagulation-flocculation dose not play a direct role in removal of ammonia (De Renzo, 1978).

Ammonium recovery was tested with Liqui-Cel 3M membrane contactor. The membrane contactor was not suitable for our pre-treated effluent (< 200 mg SS/l) although the first experiment with Liqui-Cel 3M membrane contactor did not show clogging. This might be due to small volume of sample i.e. 5 liters. The ammonia recovery was estimated 78% and removal was 86%. Amaral *et al.*, (2016) used a hydrophobic hollow fiber membrane to remove and recover ammonia from landfill leachate. They removed 99.9% of ammonia nitrogen and recovered 79.1% of ammonia nitrogen.

Pilot scale NPHarvest technique gives 82% suspended solid removal from 0.9 - 1.6 g SS/l in reject water. The liquid waste qualities vary depending on the technique involved in treatment process. Latvala, (2009) has reported in Finland reject water producing from co-digestion have average 3.9 g SS/l and wastewater treatment plant digestion have average 6.2 g SS/l. NPHarvest technique still need several samples testing from different plants.

6.5 Present status and future direction of NPHarvest technology

This section covers the research question 5. NPHarvest technology is a technique to treat LW where nutrients are recovered and recycled. The technology can be applicable to most of the liquid waste, but the chemical dosing might differ to the source of liquid waste. Using a coagulant and a polymer is a traditional way of removing organic matter from liquid waste. NPHarvest technology was applied with ballasted sedimentation technique to rapid gravity sedimentation. The pilot plant used LKD instead of micro-sand. LKD applied in pre-treatment was collected in sludge liquor does not need to be recycled (Reuillard, *et al.*, 2018). The use of sludge liquor needs further study to make acceptable as fertilizer. Sludge liquor as a by-product from the pre-treatment contains 1.3 % total solid. The sludge liquor contents mostly LKD with inorganic matter, organic matter and trace amount of phosphorus, potassium, and magnesium, is useful for plant growth. Further research on the use of lime dominant sludge as fertilizer is on-going by NPHarvest researchers.

Nutrient recovery unit uses a hydrophobic membrane, which is still in the developmental process. The use of a hydrophobic membrane in liquid-liquid is not a common technique (Amaral *et al.*, 2016). A big drawback of using a membrane is fouling of the membrane. The efficiency decreases with time. The membrane leakage can cause the mixing of extraction solution/acid and the feed-water. Washing a membrane will be extra expenses. NPHarvest nutrient recovery unit consumes less energy compared to biological treatment of WWTP. The effluent from the NPHarvest nutrient recovery unit had pH >11. It can be redirected to influent of WWTP which can reduce the calcium hydroxide dose in primary treatment. This effluent

can also use to neutralize acidic soil. The biological treatment operation of wastewater treatment results in the direct emissions of greenhouse gases (Carbon dioxide, methane, and nitrous oxide) (Campos *et al.*, 2016). Now the conventional nitrification-denitrification seems the high capital cost due to clean gaseous streams containing greenhouse gas (GHG). However, today's challenges are under the sustainability of WWTP's in terms of economic feasibility and environmental impact (Campos *et al.*, 2016). With regards to energy consumption NPHarvest technique consumed 5.4 kWh energy to treat 1 m³ reject water of Viikinmäki. The wastewater treatment cost may vary on the location and quality of liquid waste. Kaljunen, (2018) reported in his master thesis that some biogas plant, expense 10 -20 €/kg-N removal to treat their liquid waste. Comparing the liquid waste treatment cost used by NPHarvest with other industrial scale supports economically feasible in upscaling to industrial scale.

In the future, technology will be applied to the treatment process to various types of liquid waste. NPHarvest research group are working on to build suitable membrane reactor for the NPHarvest pilot plant.

7. Conclusion

NPHarvest technique is applicable to treat the wide range of liquid waste. This study designed and successfully constructed a continuous flow pilot scale pre-treatment unit for NPHarvest technique. The pilot plant with a capacity of 100 l/hr. flow rate was tested with reject water of Viikinmäki. The conversion of pretreatment from a batch test to the continuous process shows possible and feasible to develop for the industrial scale. The optimal dose of coagulant (PAX XL 100), polymer (Super floc A120) and lime kiln dust (LKD) in pretreatment: 1.3 g/l, 1.3 mg/l, and 3.5 g/l was valid when the influent suspended solid concentration was in range of 0.9 -1.6 g /l. The chemical optimization for the continuous process results in 30 % less coagulant (PAX-XL100) and polymer (Super floc A120) was compared with report 1D (Reuillard, *et al.*, 2018).

The pre-treatment unit of NPHarvest technique uses ballasted-flocculation which removed suspended solid 82%, total phosphorus 81%, and no loss of ammonia nitrogen. The nitrogen recovery unit i.e. Liqui-Cel 3M membrane contactor recovered 78% and removed 86% of the ammonia nitrogen. The drawback of using Liqui-Cel 3M membrane contactor is the need for a pre-filtration of the feed-water before passing through the contactor. This membrane contactor is not suitable for our purpose.

Estimated for the energy used in maintaining the flow and chemical dose in NPHarvest technique was 5.4 kWh/ m³ of reject water. The total cost to treat 1 m³ reject water using NPHarvest technique cost 3.18 € and 5.10 €/kg NH₄-N recovery.

References

- Aguilar, M.I., Saez, J., Llorens, M., Soler, A. and Ortuno, J.F. (2002). Nutrient removal and sludge production in the coagulation–flocculation process. *Water research*, 36(11), pp.2910-2919.
- Aho, M., Pursula, T., Saario, M., Miller, T., Kumpulainen, A., Päällysaho, M. and Descombes, L. (2015). The economic value and opportunities of nutrient cycling for Finland. *Helsinki: Sitra*.
- Akunna, J. C. (2015). 19- Anaerobic treatment of brewery wastes. Woodhead publishing series in food science, technology and Nutrition. *Brewing Microbiology*, pp 407-424, <https://doi.org/10.1016/B978-1-78242-331-7.00019-8>
- Amaral, M., Magalhães, N.C., Moravia, W.G. and Ferreira, C.D. (2016). Ammonia recovery from landfill leachate using hydrophobic membrane contactors. *Water Science and Technology*, 74(9), pp.2177-2184.
- Arnold, E., Böhm, B. and Wilderer, P.A. (2000). Application of activated sludge and biofilm sequencing batch reactor technology to treat reject water from sludge dewatering systems: a comparison. *Water Science and Technology*, 41(1), pp.115-122.
- Bachmann, S., Uptmoor, R. and Eichler-Löbermann, B. (2016). Phosphorus distribution and availability in untreated and mechanically separated biogas digestates. *Scientia Agricola*, 73(1), pp.9-17.
- Braber, K. and Novem, B. V. (1995). Anaerobic digestion of municipal solid waste: A modern waste disposal option on the verge of breakthrough. *Biomass and energy*, vol. 9, pp. 365-376
- Butler, A. (2017). Delivering precision to be continued? Batch vs. continued manufacturing [online], Orbis Biosciences. Accessed at: <https://orbisbio.com/to-be-continued-batch-vs-continuous-manufacturing/>, Accessed on 04.02.2019.
- Campos, J.L., Valenzuela-Heredia, D., Pedrouso, A., Val del Rio, A., Belmonte, M. and Mosquera-Corral, A. (2016). Greenhouse gases emissions from wastewater treatment plants: minimization, treatment, and prevention. *Journal of Chemistry*.
- Christensen, T.H. (2011). Solid Waste Technology & Management. *John Wiley & Sons*, Volume 2. 1052 p. Book, ISBN: 978-1-4051-7517-3.
- Cieślík, M., Dach, J., Lewicki, A., Smurzyńska, A., Janczak, D., Pawlicka-Kaczorowska, J., Boniecki, P., Cyplik, P., Czekala, W. and Jóźwiakowski, K. (2016). Methane fermentation of the maize straw silage under meso-and thermophilic conditions. *Energy*, 115, pp.1495-1502.

Crittenden, J.C., Trussel, R.R., Hand, D.W., Howe, K.J. and Tchobanoglous, G. (2005). Coagulation, mixing and flocculation in: *Water Treatment: Principles and Design*, second ed., John Wiley & Sons, New Jersey, 643-779.

De Mes, T.Z.D., Stams, A.J.M., Reith, J.H. and Zeeman, G. (2003). Methane production by anaerobic digestion of wastewater and solid wastes. *Bio-methane & Bio-hydrogen*, pp.58-102.

Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete, W., Rabaey, K. and Meesschaert, B., 2015. Global phosphorus scarcity and full-scale P-recovery techniques: a review. *Environmental Science and Technology*, 45(4), pp.336-384.

De Renzo, D.J., (1978). Nitrogen control and phosphorus removal in sewage treatment. *Noyes Data Corp.*

Dong, Y.B., Lin, H. and Huo, H.X. (2012). Effects of modification on the surface structure and application of composite environmental materials based on zeolite. *Journal of Functional Materials*, 19, p.008.

Driver, J., Lijmbach, D. and Steen, I. (1999). Why recover phosphorus for recycling, and how?. *Environmental technology*, 20(7), pp.651-662.

Erisman, J.W., Sutton, M.A., Galloway, J., Klimont, Z. and Winiwarter, W. (2008). How a century of ammonia synthesis changed the world. *Nature Geoscience*, 1(10), p.636.

Farley, K.J. and Morel, F.M. (1986). Role of coagulation in the kinetics of sedimentation. *Environmental science & technology*, 20(2), pp.187-195.

Finnish water utilities association (VVO). (2018). Finnish Industrial Wastewater Guide – conveying non-domestic wastewater to sewers. Helsinki: Helsinki regional environmental services authority, Publication series no. 69, ISBN 978-952-6697-38-3 (pdf).

Floudas, C.A. and Lin, X. (2004). Continuous-time versus discrete-time approaches for scheduling of chemical processes: a review. *Computers & Chemical Engineering*, 28(11), pp.2109-2129.

Ghanem, A.V., Young, J.C. and Edwards, F.G. (2007). Mechanisms of ballasted floc formation. *Journal of Environmental Engineering*, 133(3), pp.271-277.

Guo, C.H., Stabnikov, V. and Ivanov, V. (2010). The removal of nitrogen and phosphorus from reject water of municipal wastewater treatment plant using ferric and nitrate bio reductions. *Bioresource technology*, 101(11), pp.3992-3999.

Hanchang, S.H.I. (2009). Industrial wastewater-types amounts and effects. Point sources of pollution: Local effects and their control, 2, p.191.

- HSY, (n.a). Viikinmäki waste water treatment process. Viikinmäki wastewater treatment plant. Accessed at: https://www.hsy.fi/sites/Esitteet/EsitteetKatalogi/viikinmaki_tekninenesite_en.pdf, Accessed on 10.05.2018.
- Hunt, J.R., 1982. Self-similar particle-size distributions during coagulation: theory and experimental verification. *Journal of Fluid Mechanics*, 122, pp.169-185.
- Janus, H.M. and van der Roest, H.F. (1997). Don't reject the idea of treating reject water. *Water Science and Technology*, 35(10), pp.27-34.
- Jenicek, P., Svehla, P., Zabranska, J., LeBlanc, R.J., Laughton, P.J. and Tyagi, R. (2007). Reject water treatment by nitrification/denitrification process—influence of ammonia concentration and loading rate. *Water Science and Technology*, 55(6), pp.683-690.
- Kaljunen, J., Mikola, A., Pradhan, S., and Vahala, R. (2018). Nitrogen and Phosphorus harvesting from Liquid waste using hydrophobic gas permeable membrane: NPHarvest- Technical report 1b/2018. Department of Built Environment, Aalto University, pp. 54
- Kang, G.D. and Cao, Y.M. (2014). Application and modification of poly (vinylidene fluoride) (PVDF) membranes—a review. *Journal of membrane science*, 463, pp.145-165.
- Kemira, (2016). Safety data sheet- Super flocc A-120, Kemira Oyj, Helsinki, Finland.
- Lapointe, M. and Barbeau, B. (2016). Characterization of ballasted flocs in water treatment using microscopy. *Water research*, 90, pp.119-127.
- Latvala, M. (2009). Paras käytettävissä oleva tekniikka (BAT) Biokaasun tuotanto suomalaisessa toimintaympäristössä. *Suomen Ympäristö*, 24. 114p. ISBN: 978-952-11-3497-5. ISSN: 1238-7312.
- Li, Y., Park, S.Y. and Zhu, J. (2011). Solid-state anaerobic digestion for methane production from organic waste. *Renewable and sustainable energy*, 15(1), pp.821-826.
- Lime for everyday life: Limestone is an essential raw material, Nordkalk, [online]. Accessed at: <http://www.nordkalk.com/applications/agriculture/>, Accessed on 10.01.2019.
- Luning, L., Van Zundert, E.H.M. and Brinkmann, A.J.F. (2003). Comparison of dry and wet digestion for solid waste. *Water science and technology*, 48(4), pp.15-20.
- Mehta, C.M., Khunjar, W.O., Nguyen, V., Tait, S. and Batstone, D.J. (2015). Technologies to recover nutrients from waste streams: a critical review. *Critical Reviews in Environmental Science and Technology*, 45(4), pp.385-427.
- Nazaroff, W. W. and Alvarez-Cohen, L. (2001). Environmental engineering Science, Book, Wiley, pp. 690, ISBN= 9780471144946

Petzet, S., Peplinski, B. and Cornel, P., (2012). On wet chemical phosphorus recovery from sewage sludge ash by acidic or alkaline leaching and an optimized combination of both. *Water research*, 46(12), pp.3769-3780

Pitman, A.R., (1999). Management of biological nutrient removal plant sludge's—change the paradigms? *Water Research*, 33(5), pp.1141-1146.

Pradhan, S., Mikola, A., and Vahala, R. (2018). Nitrogen and Phosphorus harvesting from Liquid waste using hydrophobic gas permeable membrane: NPHarvest- Market potential 1a/2018, Department of Built Environment, Aalto University, pp. 18

Reuillard, S., Mikola, A., and Vahala, R. (2018). Nitrogen and Phosphorus harvesting from Liquid waste using hydrophobic gas permeable membrane: NPHarvest- suspended solid separation 1D72018, Department of Built Environment, Aalto University, pp. 38

Sahu, O.P. and Chaudhary, P.K. (2013). Review on chemical treatment of industrial wastewater. *Journal of Applied Sciences and Environmental Management*, 17(2), pp.241-257.

Sedimentation Process, n.d., International water association, News, Accessed on:10 August 2018, Accessed at: < <https://www.iwapublishing.com/news/sedimentation-processes> >.

Sinha, S., Yoon, Y., Amy, G., Yoon, J. (2004). Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, *Chemosphere* 57, 1115-1122

Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2003). Wastewater engineering treatment and reuse (No. 628.3 T252s). Boston, US: *McGraw-Hill Higher Education*.

Tomperi, J., Koivuranta, E., Kuokkanen, A. and Leiviskä, K. (2017). Modelling effluent quality based on a real-time optical monitoring of the wastewater treatment process. *Environmental technology*, 38(1), pp.1-13.

Tu, C., Wang, S., Qiu, W., Xie, R., Hu, B., Qu, G. and Ning, P. (2016). Phosphorus Removal From Aqueous Solution By Adsorption Onto La-modified Clinoptilolite. In *MATEC Web of Conferences* (Vol. 67, p. 07013). EDP Sciences.

Volcker, E.I., van Loosdrecht, M.C. and Vanrolleghem, P.A. (2006). Continuity-based model interfacing for plant-wide simulation: A general approach. *Water research*, 40(15), pp.2817-2828.

Ye, Y., Ngo, H.H., Guo, W., Liu, Y., Li, J., Liu, Y., Zhang, X. and Jia, H. (2017). Insight into chemical phosphate recovery from municipal wastewater. *Science of the Total Environment*, 576, pp.159-171.

Young, J.C. and Edwards, F.G. (2003). Factors affecting ballasted flocculation reactions. *Water Environment Research*, 75 (3), 263-272. doi: 10.2175/10614300 3X141051

Yuan, M.H., Chen, Y., Tsai, J.Y. and Chang, C.Y. (2016). Ammonia removal from ammonia-rich wastewater by air stripping using a rotating packed bed. *Process Safety and Environmental Protection*, Volume 102, Pages 777-785, ISSN 0957-5820,

Zhang, L., Lee, Y.W. and Jahng, D. (2012). Ammonia stripping for enhanced bio-methanization of piggery wastewater. *Journal of hazardous materials*, 199, pp.36-42.

3M Liqui-Cel membrane Contactor, (n.d.). A high level of consistency and control. Inside the Technology. North Carolina, USA.

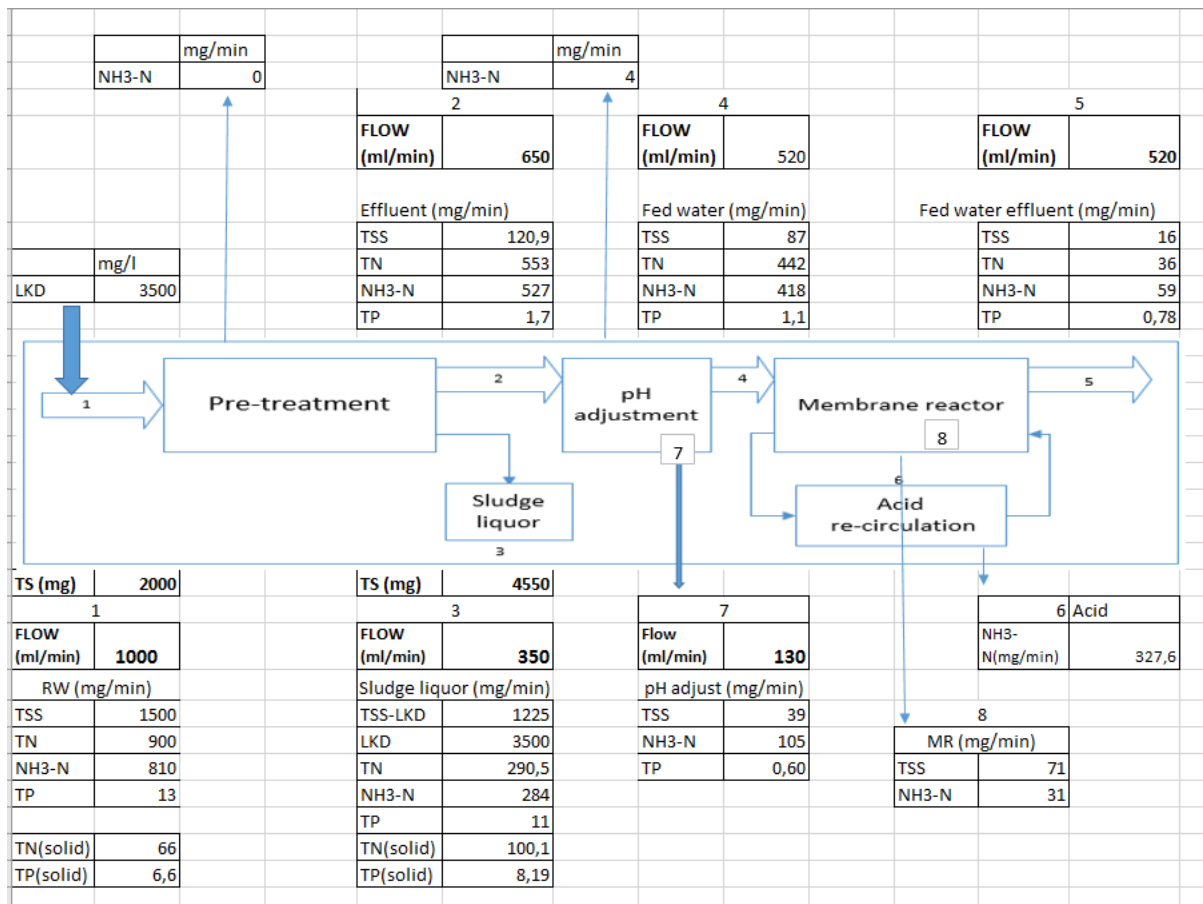
APPENDIX

Appendix 1

Dimensioning for Rapid mixing tube		
Rapid mixing Tube diameter	3	cm
Circle disc diameter	3	cm
Circular disc height	0,6	cm
Influent flow	1700	ml/min
Volume in 15 sec	425	ml
1 circular disc volume	4,24	ml
6 circular disc volume	25,46	ml
Total volume (15 sec flow + 6 circular disc)	450,46	ml
Rapid mixing tube Length	35,83	cm

Appendix 2

The mass balance of nutrients and suspended solid are estimated on the basis of mass flow. The value presented in table are the average sum from set of experiment samples. The results presented are from optimal chemical dose.



Mass balance of solid and nutrient removal and recovery during pre-treatment and nutrient harvesting

Appendix3

H2SO4 and NaOH consumption calculation for nitrogen recovery

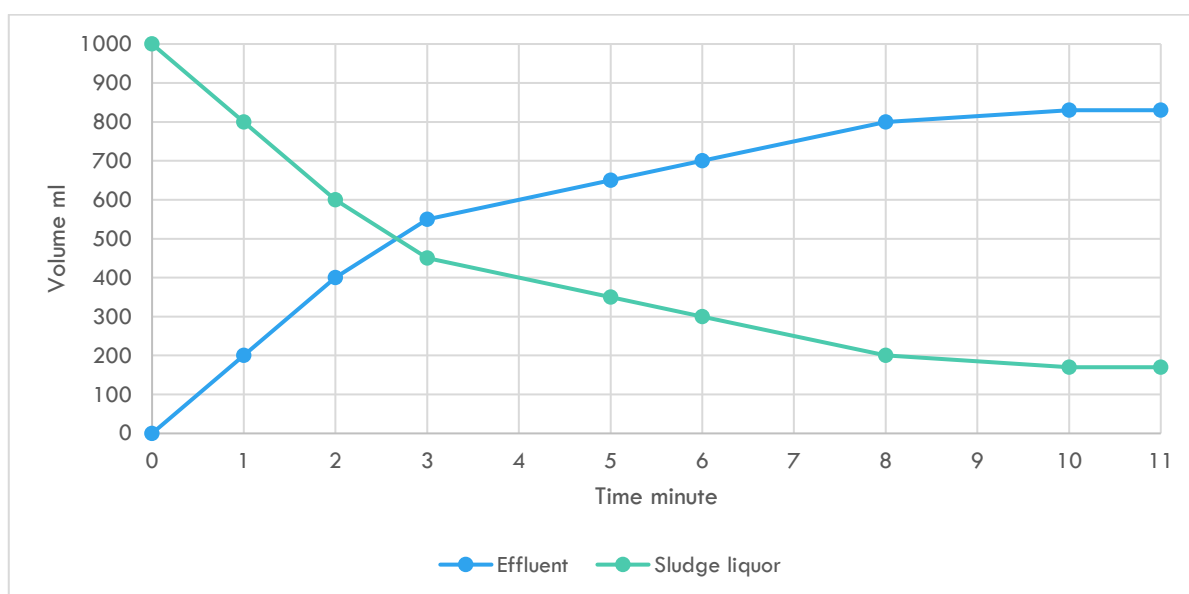
H2SO4 consumption for 1 m ³ feed-water		
Volume of feed-water	1000	L in 10 hr.
Ammonia concentration	800	mg/l
Total ammonia	800	g
Molecular wt. of ammonia	17	g
moles of ammonia in feed-water	47.06	mole
2 moles of ammonia will neutralize 1 mole of pure Sulphuric acid		
H2SO4	23.53	mole
Molecular wt. of ammonia	98.08	g/mole
mass of H2SO4	2307.76	g
conc. H2SO4 is at 98% purity		
Specific gravity of the conc. acid H2SO4 is	1.84	g/ml
Volume of H2SO4	1254.22	ml
Adjusting for the 98% purity		

Volume of H ₂ SO ₄	1279.82	ml
--	---------	----

NaOH consumption for 1 m ³ pre-treated water		
Effluent volume	1000	l
We use NaOH (4M NaOH/L)	26	ml
4M NaOH contains	160	g/l
26 ml of 4M NaOH contains	4.16	g
NaOH amount needed for 1 m ³ effluent-1	4160	g

Appendix 4

Using optimal chemical dosing in 1-liter reject water. The graph presents flocs settling time in pre-treatment.



Settling time graph of flocs in Jar test

In jar test, a clear separation of effluent and sludge liquor (E/SL = 80 /20 %) seen within 8 minutes. In continuous flow, floc settling efficiency decreased. Pilot plant have settling tank with 10 l capacity. With 1.5 l/min influent flow, the retention time of settling tank is approx. 7 min. In jar test we can achieve 65/35 % of E/SL in 5 min but due to turbulence we set this outflow ratio for pilot plant.